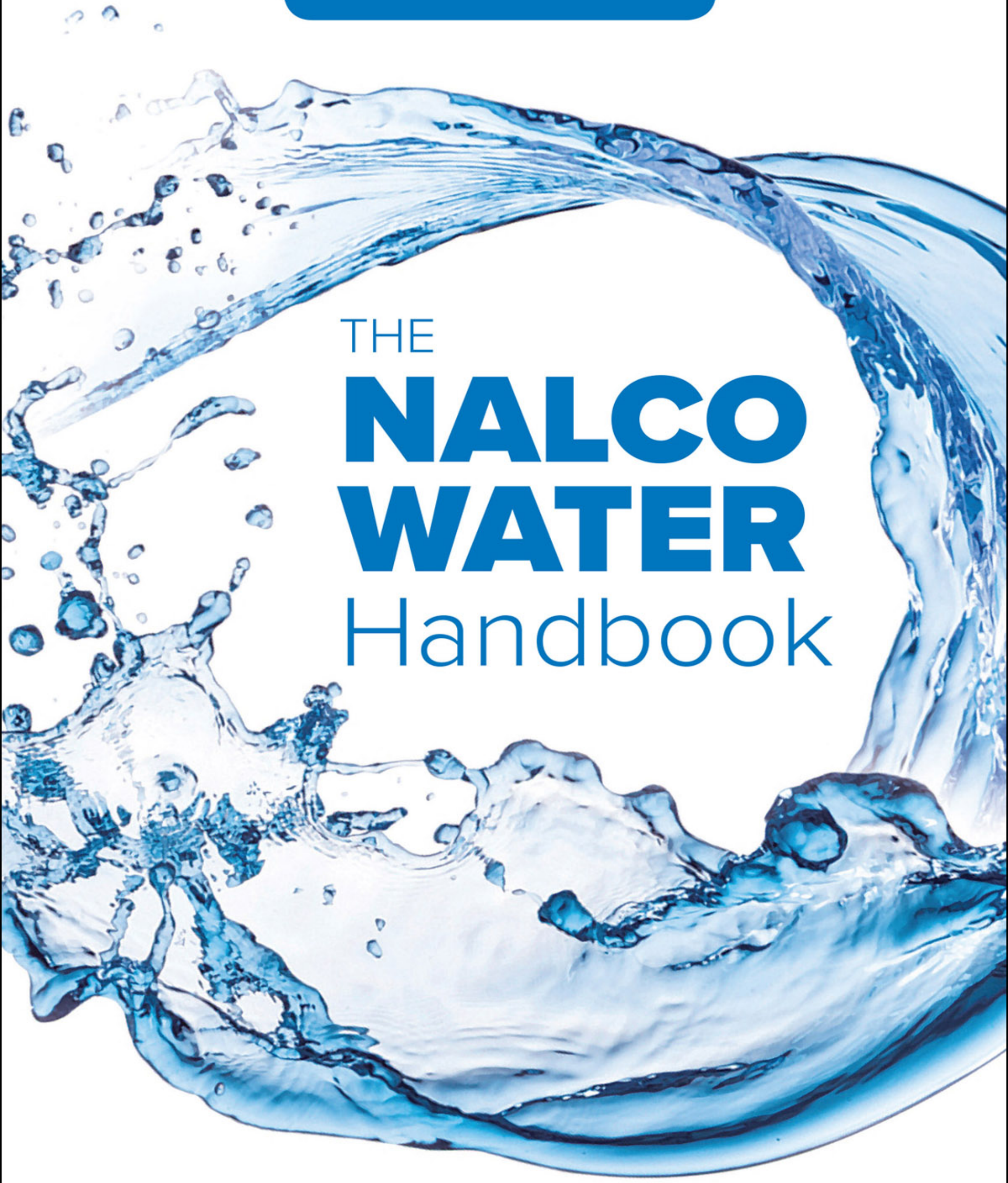
FOURTH EDITION



THE NALCO WATER Handbook

McGraw Hill Education

NALCO Water
An Ecolab Company

The Nalco Water Handbook

About Nalco Water, an Ecolab Company

Nalco Water, an Ecolab company is the global leader in water, hygiene, and energy technologies and services that protect people and vital resources. Ecolab delivers comprehensive solutions and on-site service to ensure safe food, maintain clean environments, optimize water and energy use, and improve operational efficiencies for customers in the food, healthcare, energy, hospitality, and industrial markets in more than 170 countries around the world.

The Nalco Water Handbook

Nalco Water, an Ecolab Company

Daniel J. Flynn Editor

Fourth Edition

McGraw Hill Education

New York Chicago San Francisco
Athens London Madrid
Mexico City Milan New Delhi
Singapore Sydney Toronto

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Foreword

Business and industry are increasingly identifying water scarcity as a business constraint and risk. By the year 2030, the World Economic Forum estimates that the global demand for freshwater will exceed supply by about 40%. The ever-increasing demand for freshwater is causing us to consider the potential outcomes, where water stressors start to inhibit our ability to meet the critical needs of our customers around the world. Yet the risk is not equitable across the globe. Each watershed is different. There are acute shortages in some places and not in others. We also find that universally water is underpriced, and the prices are inverse to the risk.

Our conversation is changing. We are reframing our discussion and vocabulary around water to reflect the challenges, the risk to business, and the true cost of the resource. We are finding ourselves at an inflection point. We have obtained the knowledge and sophistication to make the case for water strategies in our facilities that make good business sense, and enable growth in an environmentally sustainable and socially equitable manner. Implementing water strategies within plants needs to make good economic sense and be accomplished in a manner that allows the business a fundamental license to grow.

Our fourth edition of *The Nalco Water Handbook* opens up the discussion on water scarcity, stressors, and the business case for managing water. The content throughout the book will assist you in maintaining clean heat transfer surfaces as well as addressing water management needs through the lens of reduction, reuse between applications, and recycle. As you read through the book, look for the items that can become actionable in your facility and not just protect your assets, but that can help your water management strategies as well.

Christophe Beck
President, Nalco Water
Executive Vice President, Ecolab

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Preface

As Nalco Water approaches its 90th year in business, it seems fitting to release the fourth edition of *The Nalco Water Handbook* at the same time. Our first book, *Water: The Universal Solvent*, was published in 1977 in observance of the company's 50th anniversary. Frank N. Kemmer, editor-in-chief and John McCallion, associate editor of that book, went on to produce the first two editions of *The Nalco Water Handbook* and firmly placed Nalco Water well down the road of knowledge sharing. We at Nalco Water continue to believe this is as important today, as it was when the first book was published.

Water as a resource is becoming increasingly scarce throughout much of the world. In this edition of the book, we have restructured the initial introductory chapters through the lens of water scarcity, stressors, and business risk. In addition, we have added supplementary content around water conservation in various processes where applicable. We have also strengthened the discussions around various industry processes, impurity removal with membrane technology and water safety for building water systems. Finally, we have added additional chapters in the industry section to broaden the scope of the discussion.

We have made liberal use of tables, illustrations, photographs, and line drawings to help place the discussion in context. Hundreds of graphics have been refreshed to assist in clarifying the message they convey. The changes we have made to the content and the presentation should make this book valuable across a wide range of users such as plant operators, engineering departments, process management, maintenance groups, and plant mangers to name a few.

Daniel J. Flynn
Editor

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Acknowledgments

When we were evaluating the updating, and refreshing of this text, it became very clear quite early on that we would be asking a good number of people for contributions of time, text, photographs, drawings, illustrations, fact checking, and numerous reviews just to mention a few of the items. As the project progressed, the numbers grew as we cast our net further into the many disciplines and departments throughout Nalco Water. We would like to take this opportunity to acknowledge the participation and efforts of the individuals involved with the fourth edition of *The Nalco Water Handbook*.

The following individuals made significant contributions of writing, reviewing, fact checking, and generally ensuring the content of the book remains best in class for this fourth edition, as well as the previous third edition. It is with great thanks that we acknowledge their efforts. Alex Glass, Amit Gupta, Andrew Cooper, Andrew Hook, Anton Banweg, Barbara Moriarty, Ben Riley, Blaine Krause, Bob Pomeroy, Bonnie Harris, Brad Benz, Brian Jenkins, Carl Rossow, Carolina Diaz-Rodriguez, Carolyn Will, Christine Staples, Chuck Foster, Cindy Ojczyk, Daniel Flynn, Daniel Meier, Debbie Bloom, Dennis Martin, Don Roll, Donald Johnson, Ed Swenson, Emilio Tenuta, Eric Kangas, Eric Myers, Flora Lu, George Peabody, George Totura, Greg Coy, Gregg Galbreath, Heidi Olszewski, Howard Barnes, James Gage, Jane Kucera, Janet Kirkman, Jasbir Gill, Jason Burney, Jason Van't Hul, Jeffrey Oloier, Jim Dillon, Jim Haff, John Sparapany, Jorvic Vital, Ken Fulks, Ken Voytell, Kevin Gehan, Kevin Kaiser, Kirby Lee, Larry Hill, Leroy Swenson, Melissa Callejo, Michael Lesniak, Michael Martin, Mike Backode, Mike Vittum, Mita Chattoraj, Nancy Stan, Patrick Miller, Paul Desch, Paul Williams, Peter Hicks, Peter TenEyck, Ram Nagarajan, Richard Jacobs, Rick Lyons, Rob Henderson, Robert Wetegrove, Ronald Kochik, Ronald Tebbetts, Sam Lordo, Scott McLaughlin, Seth Werlinsky, Sherri Binetti, Steff Vrijhoeven, Steve Andrick, Steven Kramarczyk, Sue Molloy-Vesley, Tammy Lai, Tim Keizer, Tom Lindley, Tracey Guddendorf, Walter Schaefer, and so many others who touched this project in various ways.

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Daniel J. Flynn
Editor

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SECTION 1

Introduction

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CHAPTER 1

The Business Case for Managing Water

Water—we take it for granted in much of the world. To be sure, it comprises fully three-quarters of the surface of the earth. We build our cities close to it. Vacations are planned to include it. Water's domestic use is critical to our survival. It is fundamental to the portion of our economy that is agrarian in nature. It is important for much of our industrial processes. With so much of the earth covered with water and it being fundamental to our industry, agriculture, and life, humankind has undertaken to utilize water in many different ways to suit our needs and desires.

Despite our reliance on water, there has been no incentive to value it for the precious and limited resource that it is. The world is changing. It is growing, more urban and affluent. These populations are demanding more resource-intensive goods and services. These changing global dynamics are placing increasing pressure on the world's diminishing freshwater supplies. For industry to be sustainable for the long term, mindsets and practices related to water must change.

While a significant portion of our planet is covered with water, most of it is not usable in the form we find it. For human use, we look to break water into two groups, fresh and salt. Human use is centered on freshwater, which comprises only about 2.5% of all the water found on earth. The remaining 97.5% is considered sea or saltwater. Saltwater is not considered suitable for industry, agriculture, or domestic use.

When we look at the freshwater resources on earth, we find that an estimated 68.7% of it is locked in ice sheets and glaciers at our poles, on mountaintops as glaciers and snow pack, and in the ground as permafrost. These resources are considered out of our reach and therefore unusable as they sit. This leaves us a very small 1.2% of

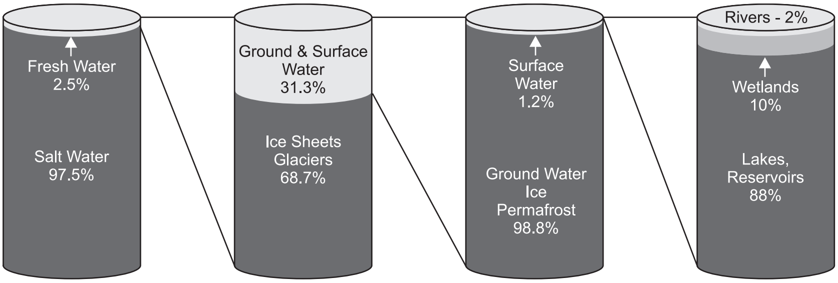

FIGURE 1.1 Breakdown of earth's water resources, illustrating freshwater components by percentage.

the water on earth as usable surface water or groundwater. This fraction of the earth's water resources supports all terrestrial life and powers our industries. This thin 1% sliver of water is our focus in this book (Fig. 1.1).

Global Trends Affecting Water Supply

The Impact of Climate Change on Glacial Water

Our planet is warming. The effect on weather patterns varies across the world, but the effect on ice packs and glaciers is known: They are melting. This melting does not always result in usable freshwater. Sea icepacks and tidewater glaciers such as those found in the Antarctic break off and melt directly into oceans (Fig. 1.2).

FIGURE 1.2 The Hubbard Glacier in Alaska is a tidewater glacier that terminates in Yakutat Bay in the Gulf of Alaska. (*Courtesy of D.J. Flynn.*)

Figure 1.3 The Mendenhall Glacier in Alaska is a valley glacier feeding Mendenhall Lake and Mendenhall River. (*Courtesy of A.C. Van Sistine.*)

Mountain or valley glaciers that do not terminate at the ocean are the headwater sources for many of the earth's major rivers. These rivers depend on sufficient snowfall in mountain regions to maintain the glaciers and provide sufficient melt water for yearlong river water flow. As these glaciers retreat, the amount of reserve capacity is decreasing, threatening to turn yearlong rivers into seasonal water sources. Since we rely on these surface waters, the effect of climate change on glaciers creates water stress to downstream consumers (Fig. 1.3).

Technology has enabled municipalities and industries to access underground reservoirs, or groundwater, which constitutes more than 90% of the total freshwater available for human use. Without sustainable replenishment, groundwater extraction is a short-term solution that adds to the stress on those water sources as well.

Impact of Population Trends on Surface and Groundwater

Global trends, including shifts in population growth, and increasing demand for water, food, and energy are impacting all facets of our world economy. Here are a few emerging macro trends from the United Nations and other organizations worth noting:

- The world's population is predicted to expand to 9.7 billion by 2050.[1]

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[1] United Nations Department of Economic and Social Affairs, *World population projected to reach 9.7 billion by 2050*, July 29, 2015, http://www.un.org/en/development/desa/news/population/2015-report.html.

- By 2025, 90% of population growth will be in developing or emerging markets. Urban populations are expected to rise from 3.9 to 6.4 billion, accounting for 67% of the world's population, with nearly 90% of the increase in Asia and Africa.[2]
- In the next 20 years, there will be three billion more middle-class consumers, increasing demand for goods and services and putting unprecedented pressure on the world's limited natural resources.[3]
- Increased pollution from municipal and industrial waste and the leaching of fertilizers and pesticides used in agriculture will all contribute to shrinking the world's potential freshwater for human and industrial needs.

Climate change and population growth are the two main stressors on the global freshwater supply. The agriculture, energy, and manufacturing sectors will all need to challenge their industries to rethink their processes in order to reduce water consumption and remain viable. According to the United Nations World Water Development Report, reconciling different water uses at the surface and groundwater level and improving policy coherence nationally and across borders will be priorities for many years to come.[4]

Sustainability as a Business Driver

The original definition of sustainability from the Brundtland Report reads: involving development that meets the needs of the present without compromising the ability of future generations to meet their own needs. For businesses, this means achieving sustainable, sound growth while minimizing risk and natural resource consumption. Another way to say this is, "doing more with less."

Companies adopting sustainable business practices understand that they are most successful when economic and environmental benefits align. Measuring the link between performance outcomes, environmental impact, and cost savings demonstrates the value of operating sustainably and helps make the business case for water-saving solutions.

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[2] United Nations, *World Urbanization Prospects, The 2014 Revision,* United Nations, New York, 2014, https://esa.un.org/unpd/wup/Publications/Files/WUP2014-Highlights.pdf.

[3] Dobbs, R., Oppenheim, J., Thompson, F., Brinkman, M., Zornes, M., *Resource Revolution: Meeting the World's Energy, Materials, Food, and Water Needs*, McKinsey Global Institute, November, 2011, http://www.mckinsey.com/business-functions/sustainability-and-resource-productivity/our-insights/resource-revolution.

[4] UN-Water, *The United Nations World Water Development Report 2015 Water for a Sustainable World*, United Nations Educational, Scientific and Cultural Organization, Paris, France, 2015, http://unesdoc.unesco.org/images/0023/002318/231823E.pdf.

Progressive companies are setting more and more aggressive sustainability goals and publicly reporting progress against those goals. These commitments are good for both business and society. For more than a decade, the United Nations (UN) Global Compact-Accenture Strategy have compiled research from leading CEOs around the world and across a diverse set of industries as they are called to take action on their sustainability goals. A UN Global Compact-Accenture Strategy CEO Study of more than 1000 CEOs conducted in 2016 reports that 89% of industry leaders said their commitment to sustainability is translating into real impact in their industries.[5] In this same study, 59% report their company is able to accurately quantify the business value of their sustainability initiatives, up from 38% in 2013. The report further states that business leaders are still looking for additional ways to measure, track, and communicate the impact of sustainability on metrics of business success, and demonstrate their impact on corporate sustainability goals. Growing pressure from consumers, investors, and reporting agencies is starting to mobilize the business world, with increasing urgency and conviction.

Sustainability Reporting and Regulations

In response, a new trend has emerged: increased proactive, voluntary reporting on water and energy use and other sustainability metrics. Table 1.1 includes some of the leading globally recognized reporting standards through which businesses are able to demonstrate their sustainable performance. They are also utilized to hold businesses accountable for reporting on their sustainable performance.

Companies committed to public reporting recognize that benefits can include increased share value and investor confidence; increased stakeholder engagement, support and patronage; increased staff motivation, confidence, and productivity; innovation in new products and market development; and increased profitability through cost reductions consequent on consuming fewer resources, creating less waste for disposal, reduced emissions, and better management of cash flow. Many companies are now positioning their business on a platform of sustainable development that visibly proclaims what they stand for and how they are contributing to their own and their customers' sustainability goals.

Companies around the world are also facing increasing regulations in the form of legislation and controls that govern their operations and how they impact the environment and society. For example, where wastewater was an inexpensive output of industry in the past,

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[5] Accenture Strategy, *Agenda 2030: A Window of Opportunity*, The UN Global Compact-Accenture Strategy CEO Study 2016, https://www.accenture.com/us-en/insight-un-global-compact-ceo-study.

Reporting Standard	Organization	Summary
GRI G4 Sustainability Reporting Guidelines	Global Reporting Initiative	Globally accepted framework for reporting sustainability metrics
CDP Water Program	CDP	Framework for reporting water usage information
UN Global Compact Communication on Progress (COP)	United Nations	Framework for reporting sustainability performance as it aligns with UNGC Ten Principles
Dow Jones Sustainability Index	S&P Dow Jones Indices and RobecoSAM	Family of indices evaluating the sustainability performance of largest 2,500 companies listed on Dow Jones Global Total Stock Market Index
Corporate Sustainability Reports	Organization	Platform used by organizations to communicate sustainability performance and impacts

Table 1.1 Globally Recognized Reporting Standards for Sustainability Metrics

more stringent regulations are resulting in increasing costs to clean water for discharge back to the environment.

Within the European Union (EU), legislation such as the Integrated Pollution Prevention and Control (IPPC) regulations; the Biocidal Products Directive; and the Registration, Evaluation, Authorization, and restriction of Chemicals regulations (REACH) have demonstrated a strong commitment to control how companies are expected to protect the environment and human health. Availability of data has revolutionized ways in which regulations are applied and monitored. For example, the Toxic Release Inventory (TRI) operated by the U.S. Environmental Protection Agency (EPA) is a public database listing by company, containing the known releases of chemicals to the environment. The European Pollutant Release and Transfer Register (E-PRTR) have now joined the EPA in making pollution and emission data freely available to all citizens. The Pennsylvania Department of Environmental Protection (PADEP) has mapped all the waterways in the U.S. state of Pennsylvania. The PADEP uses the Pennsylvania Single Discharge Waste Load Allocation Program for Toxics and Other Substances (PENTOXSD) water quality analysis application to determine permit limits for toxics and certain other substances. In addition, enforcement agencies in many countries around the world publish data on emissions that affect their specific territories.

Industrialized western countries generally led the way with regulations on waste discharge. Today, emerging countries around the world are following suit and beginning to regulate or enforce laws around waste discharge back to surface waterways. Increased regulation will start to reduce the pollutant load on surface waterways and help ensure that water continues to remain usable downstream from discharge points. This means there will be an increased need for equipment and chemistry to treat waste streams and make water suitable for discharge. Countries like China, India, and many of the countries in Eastern Europe are beginning to strengthen discharge requirements for municipal and industrial processes. China, for example, launched a new environmental protection law (EPL) in 2015 with details on harsh penalties for environmental offenses and provisions for tackling pollution and raising public awareness about offenders.

Making the Business Case for Managing Water

The future of freshwater availability is uncertain. According to the World Economic Forum, global water crises are a threat of highest concern for the next 10 years.[6] As stated earlier, only a very small percentage of the world's freshwater supply is readily accessible for direct human use. Implications for businesses, communities, and individuals are real, and supplies are limited. The following statistics frame this era of freshwater scarcity:

- 36 countries face extremely high levels of baseline water stress, whereby more than 80% of available water is withdrawn annually.[7]
- By 2025, water withdrawals are predicted to increase by 50% in developing countries and 18% in developed countries.[8]
- 47% of the world's population will be living in areas of high water stress by 2030.[9]

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[6] Ganter, C., *Water crises are a top global risk*, World Economic Forum, Jan 16, 2016 https://www.weforum.org/agenda/2015/01/why-world-water-crises-are-a-top-global-risk/.

[7] Reig, P., Maddocks, A., Gassert, F., *World's 36 Most Water-Stressed Countries*, World Resources Institute, Dec 12, 2013, http://www.wri.org/blog/2013/12/world%E2%80%99s-36-most-water-stressed-countries.

[8] Un-Water, *Statistics detail*, The United Nations Inter-Agency Mechanism on all Freshwater Related Issues, Including Sanitation, http://www.unwater.org/statistics/statistics-detail/en/c/211816/.

[9] Organization for Economic Co-Operation and Development, *OECD Environmental Outlook to 2030*, OECD 2008, http://www.oecd.org/env/indicators-modelling-outlooks/40200582.pdf.

- By 2030, global water demand is set to overshoot supply by 40%.[10]

Policymakers and regulators have been reacting to increasing water scarcity by placing restrictions on water use in high-stress areas, as happened in 2015 in the U.S. state of California, where businesses and residents were under a mandate by the governor to reduce water consumption by 25%.

It is uncertain how much control businesses will have in the future over their ability to access the water required for their operations as water demand grows and areas of water stress expand. Limited availability or a compromise in quality can significantly disrupt operations, threaten revenue and investor confidence, curtail growth, and result in stranded assets. Businesses in water stressed areas may also face reputational risks from communities and citizens concerned about unsustainable and inequitable use of water. Businesses stand to lose control of their futures if they do not proactively manage water.

Calculate the Full Value of Water

Very few business leaders know how much water it takes to generate an hour of operation at their business. Water is typically viewed as a readily available commodity associated with an annual water bill, not a resource that is material to operation. Water conservation is low on the list of priorities for many companies because water is underpriced compared to its full value to the business, defined based on real and future risks that water scarcity poses to operations at a local level. The disconnect between the market price for water and a business's inherent water-related risks makes it hard to prioritize water in business decisions.

The first step to making the business case for water management and investment in water solutions involves assessing and monetizing water scarcity and water quality risk over time at the enterprise and facility level. One way to assess water scarcity risk is to consult with water basin maps. The Aqueduct tool by World Resources Institute (WRI) identifies overall water risk around the world through an aggregated measure of selected indicators to reflect long-term conditions (http://www.wri.org/our-work/project/aqueduct).

Another publicly available tool, the Water Risk Monetizer (WRM), uses scientific models developed by Trucost, WRI data, and site-specific data from a facility to quantify the impact of water

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[10] World Economic Forum, *Part 1—Global Risks 2015: Environment—High Concern, Little Progress,* World Economic Forum, http://reports.weforum.org/global-risks-2015/part-1-global-risks-2015/environment-high-concern-little-progress/.

scarcity and quality risk in monetary terms. It calculates a water risk premium by considering the amount of water available at a specific location, the amount of water used by a facility, incoming and outgoing water quality, projected water use over time, additional demands on the supply of water from population and GDP (gross domestic product) forecasts, and the impact of a facility's water use on the watershed. The water risk premium, when added to the local price a business pays for water, quantifies the full value a business should place on water based on real and future risk. The WRM also provides a "revenue at risk" likelihood score by estimating the value of the revenue that could potentially be lost at a facility due to the impact of water scarcity and declining water quality on operations.

Both the water risk premium and potential revenue at risk metrics are financial indicators which companies can use to inform business decisions that address water-related constraints to growth. The WRM tool provides water users with the full value of the water to an operation to help:

- Determine the water risk premium at each facility in an enterprise to understand those facilities most at risk: identify sites where water is most undervalued by calculating a risk-adjusted water price.
- Budget, plan, and develop strategies when considering return on capital expenditure and operating expenditure investments in existing facilities: facilities with the greatest gap between current price and risk-adjusted price should be prioritized.
- Calculate internal rate of return (IRR) for a site-specific water efficiency investment: by using a risk-adjusted water price instead of water costs, a company can calculate the value-based return on investment to make the case for water-saving solutions.
- Determine preferred locations for expansion projects and manage expansion into high risk areas: assess current and future water-related risks.
- Evaluate the impact on investments when considering expansion in new locations by leveraging a water risk premium in financial models [weighted average cost of capital (WACC) in new construction projects].

Monetized risk can help companies align water use with availability and evaluate new infrastructure investments, procurement strategies, innovation, and product portfolios to make business decisions that are sustainable in the long term (http://waterriskmonetizer.com/about/).

Perform a Total Plant Assessment of Water Use

Plant operators can assess how water is put to work throughout a facility to identify opportunities for water conservation. A total plant assessment should be conducted to help plant operators understand the water intensity and maximize water use reduction (efficiency). It is not uncommon for manufacturing facilities to know how much water comes into the plant and is discharged. Very few, however, know how water is being utilized or lost throughout the operation.

A total plant assessment provides data and insights to help align water intensity improvements throughout an operation with business strategies. It also reveals synergies that are often missed if solutions are focused solely on individual water saving solutions. The most common problems uncovered during total plant assessments include:

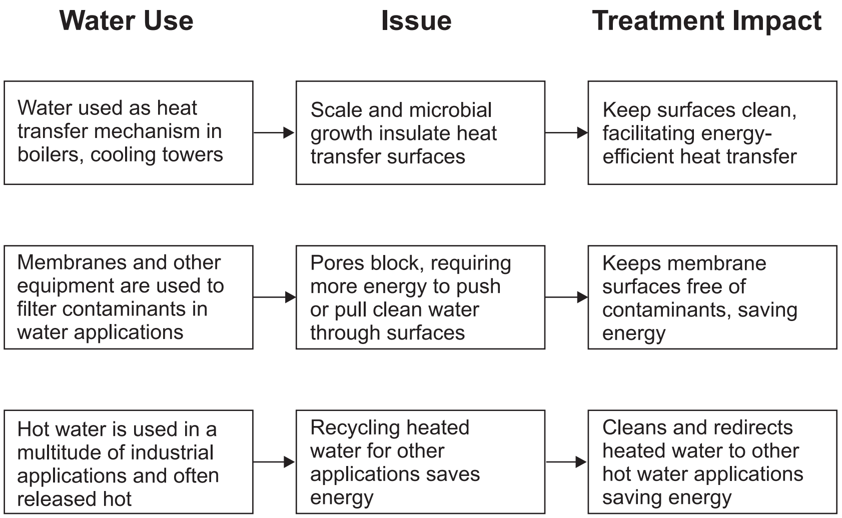
- Leaking valves
- Tanks running over
- Valves left open over a weekend or on nonproduction days
- Missed opportunities such as not repurposing clean rinse water into a cooling tower
- Machinery not operating to specification

Undertaking a total plant assessment of water use can also uncover opportunities to improve energy-related outputs. There is a very clear link between maintenance of clean heat exchange surfaces and the amount of fuel required to maintain desired heat transfer, amount of greenhouse and other gases created, and ultimately costs incurred. Likewise, the logic can be applied to many other operations, such as membrane performance and management of heated water. All of these links can be controlled to best contribute to energy and water management of the activity involved, as shown in Fig. 1.4.

Value and Prioritize

After the opportunities for water conservation have been identified and risks have been monetized, businesses can leverage the data to make the business case for improvements, measure the anticipated impact, and determine return on investment. Decision making under the new normal of increasing freshwater scarcity and declining water quality must prioritize water-saving investments that support growth. Strategic questioning helps to identify a pathway for decision making. Some of these questions include:

- What is the percentage of water used per output as a percentage of the total? This provides a “big picture” analysis to index water use based on output for a particular facility.



Water Use	Issue	Treatment Impact
Water used as heat transfer mechanism in boilers, cooling towers	Scale and microbial growth insulate heat transfer surfaces	Keep surfaces clean, facilitating energy-efficient heat transfer
Membranes and other equipment are used to filter contaminants in water applications	Pores block, requiring more energy to push or pull clean water through surfaces	Keeps membrane surfaces free of contaminants, saving energy
Hot water is used in a multitude of industrial applications and often released hot	Recycling heated water for other applications saves energy	Cleans and redirects heated water to other hot water applications saving energy

Figure 1.4 Water treatment and energy use reduction.

Whether it is water use per tons of paper or cases of soft drink, knowing how much water is required per product unit will help determine the priorities for water-saving strategies.

- How does water use per output compare to industry norms or industry benchmarks?
- What is the potential for water scarcity at the facility and what potential impact it will have on operations? This is a critical component to the overall assessment because it drives water reduction strategies for operational resiliency while also considering product quality.
- What are other businesses in the industry doing to reduce water consumption?

If water-related risks are not considered in growth strategies or properly managed, the outcome can be reduced revenues, higher operating costs, stranded assets, regulatory fines, and lower investor confidence. All these can restrict access to capital, higher financing rates, or higher insurance premiums.

Water Risk Monetizer Case Studies

The following examples depict industry-specific case studies using industry averages for costs and water risk assessments. Results from the water risk monetizer can guide businesses in their quest to measure, monetize, and manage water scarcity risks to sustain growth.

Business Expansion Projects

Scenario 1: Based largely in Southeast Asia, a company is evaluating a new strategy to increase revenues 17% by 2017. This will require a 32% increase in water use at two existing facilities in India and the addition of one Greenfield facility to come online in 2015. How do the water risk premium, other risk factors (scarcity, reputational, and regulatory), and profitability compare to business as usual?

Scenario 2: A company needs to increase production by 20% to meet demand. The company is considering two locations in India—Mumbai and Bengaluru—for a new facility to help meet increased production needs. Based on the current water risk premium, which location is preferred? Based on water scarcity risks in 10 years, which location is preferred?

Scenario 3: A company is looking to expand its operations in a new region. A water risk assessment determined that the company is targeting a high-risk water basin for its new facility location. How can the company determine the impact of this location to the company's WACC on this investment?

Existing Facility Water Improvement Projects

Scenario 1: A company is considering investing in technology to improve water use efficiency at its facility in order to reduce regulatory and reputational risk.

What would be the IRR for a facility investment designed to improve water efficiency by 27% using a risk-adjusted price of water (current price plus water risk premium)?

Scenario 2: A company uses the World Wildlife Fund (WWF) Water Risk Filter and WRI Aqueduct tools to assess and determine which existing operating facilities are operating in what are considered water scarce sweet spots. The tools identified three production facilities in a high water stress and scarcity region.

- Which facility should be the highest priority for immediate investments in water stewardship initiatives to reduce its impact on the water basin based on risk-adjusted water bills over a 3-, 5-, and 10-year period?
- What is the water risk premium at each facility and how can that information be used to prioritize investments to reduce water use?

Scenario 3: A company has identified five facilities that require water saving investments and a list of water efficiency improvement projects for these facilities.

Using a water risk premium, what would be the IRR of these improvements and how should they be prioritized?

Scenario 4: A major production change is proposed at a chemical plant that will decrease electricity use by 20% while increasing water use by 15%. The plant is located in a region of China where a carbon tax of $5 per ton is expected in the next two years.

What is the overall net change in utility cost (electricity, carbon tax, and risk-adjusted water costs)? What is the water risk and how does this compare to business as usual?

Understanding the impact—and associated costs—of these risks at the enterprise and site level, as well as the broader implications and consequences of business operations to the surrounding community, enables businesses to make more informed decisions about their water use.

Subsequent chapters of this book will address the use of water in various applications, processes, and industries, and how to manage that water to minimize consumption, lengthen equipment life, maximize intended work, and ensure proper contaminant removal before discharge.

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CHAPTER 2

Water Sources and Stressors

The water cycle (Fig. 2.1), also known as the hydrologic cycle, describes the continuous movement of water on, above, and below the surface of the earth. Water can change states becoming liquid, vapor, or ice at various stages of this cycle. These processes happen rapidly and have occurred over millions of years. The balance of water remains constant over time, but the individual water molecules transform rapidly. The sun drives the water cycle, which has no starting or ending point. The sun heats the water in the oceans, where some of it evaporates as vapor into the air. Ice and snow can sublimate directly into water vapor. Air currents take the vapor into the atmosphere along with water transpired from plants and evaporated from soil. The vapor rises into the atmosphere, where cooler temperatures cause it to condense into clouds. Air currents move clouds around the earth, where clouds collide, grow, and fade out of the sky as precipitation, which falls as rain, snow, hail, fog, and sleet. Snow can accumulate as icecaps and glaciers, which can store frozen water for thousands of years. Snowfall in temperate climates melts in spring and flows overland. Most precipitation falls back into the oceans. That which falls onto land mostly flows over the ground as surface runoff. A large portion enters rivers, which move water toward the oceans. Runoff and groundwater seepage are stored in lakes and reservoirs. A portion of water infiltrates deep into the ground and is stored in aquifers for long periods. Over time, groundwater flows back into the oceans, where the water cycle is renewed.

Water Sources

Resources of freshwater around the globe are not split evenly. Regionally, North and South America enjoy the most water, while North Africa and the Middle East have the least. When we consider resources by country, the following eight countries have roughly

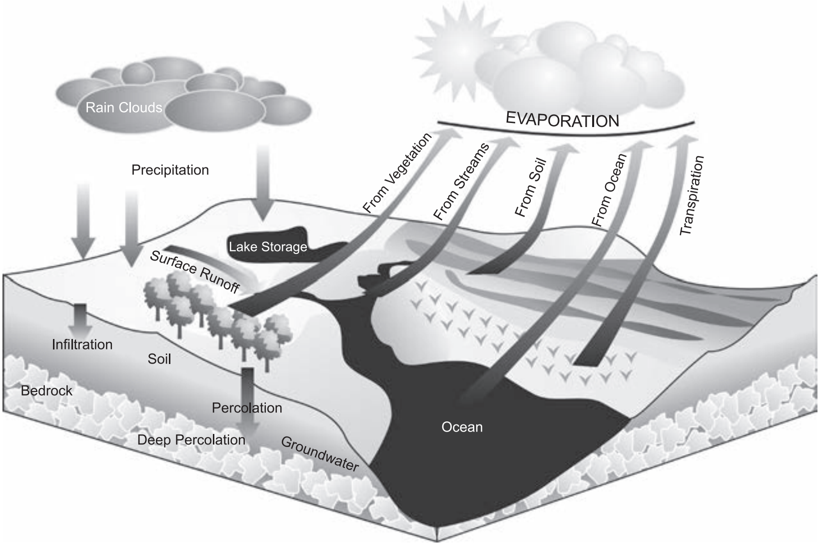

Figure 2.1 Illustration of the hydrologic cycle. (*Source: U.S. Geological Survey.*)

one-half of the renewable freshwater resources of the world: Brazil, Canada, China, Columbia, Indonesia, Peru, Russia, and United States.[1]

Location of renewable freshwater itself is only part of the equation; the balance of the equation is population density. Increasing the population density in an area of the world where renewable freshwater resources are limited creates stress on the water supply. According to the United Nations, a population experiences water stress when the water supply drops below 449 000 gal (1700 m^3) per person per year.[2] At present, roughly 40% of the world's population lives in an area that can be described as under water stress. As noted in the previous chapter, this number is expected to reach more than 47% by the year 2030. Adding to this, areas of the world that possess freshwater less than 264 000 gal (1000 m^3) per person per year are experiencing water scarcity and run the risk of food production strain and economic development difficulties. Absolute water scarcity occurs when water supplies fall below 132 000 gal (500 m^3) per person per year. At levels this low, even basic domestic needs are hard to meet. These problems can be mitigated, if the countries experiencing the issues possess the wealth to undertake and institute

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[1] Pacific Institute, *Data Table 1, Total Renewable Freshwater Supply by Country (2013 Update)*, The World's Water Volume 8, 221–226, Jan 2014 http://worldwater.org/wp-content/uploads/2013/07/ww8-table1.pdf.

[2] United Nations, *Water Scarcity*, Nov 2014, http://www.un.org/waterforlifedecade/scarcity.shtml.

newer technologies to reduce, reuse, and recycle water. Water stresses are occurring to both our ground and surface water resources.

Surface water sources include rivers, lakes, and reservoir systems. Groundwater is water stored between layers of rock or in sand beds underground. Groundwater can be removed for use from springs or wells. Cities, industries, and agriculture utilize these sources for drinking water, heating, cooling, process, food, irrigation, transportation, and commerce. This chapter will look at the general characteristics of various sources of surface water and groundwater. Analyses are included to illustrate the differences and similarities of water quality around the world. These analyses are used to determine the type and size of various water treatment schemes and equipment needed to make the water useful for the particular application.

Each continent of the world has significant rivers, lakes, and underground aquifers that provide sources of freshwater. These represent precious resources that enable humans to exist and populate certain areas of the world. In fact, the population density of the world often follows the availability of water resources; water-rich areas can support more people than arid locations. As the world population grows, freshwater resources become ever more important as the need for water also grows.

Surface Water—Rivers

Human civilization and culture developed along major rivers such as the Tigris-Euphrates, Nile, Yellow, and Ganges. Capitols of ancient empires grew and faded as conquerors marched their way across landscapes, down rivers, and overseas. The Tigris-Euphrates Rivers provided much of the water that supported the development of ancient Mesopotamic cultures of Assyria, Babylonia, and Samaria. For millennia, the Nile nurtured ancient Egyptian dynasties with its yearly floodwaters and by allowing transportation and commerce along its length. The Yellow and Yangtze Rivers in China and the Ganges River in India were the hubs of civilizations and of transportation and commerce. Later in history, abundant supplies of water attracted colonists of North America to settle along rivers.

North American Rivers

These are often navigable waterways or important sources of water for domestic use or irrigation. Major examples include the St. Laurence River connecting the Great Lakes to the Atlantic Ocean. It forms the vital link of the St. Lawrence Seaway. The Mississippi River system is another major waterway in North America, especially when combined with its two long tributaries, the Ohio and Missouri Rivers. The Tennessee River is a tributary of the Ohio River and drains much of the southeastern U.S. Combined, the Mississippi, Ohio, Missouri, and Tennessee Rivers drain the majority of Central United States.

Figure 2.2 Erosion caused by the Colorado River has contributed to the creation of the Grand Canyon in the Southwestern United States. (*Photograph by D. Dolde.*)

In the southwestern portion of the United States, the Rio Grande forms the entire border between Mexico and the state of Texas. It is a long river but has a very small flow, especially compared to the Colorado or Mississippi Rivers. The Colorado River, in the southwestern United States and northwestern Mexico, is a major water source for domestic consumption and irrigation (Fig. 2.2). Aqueducts carry its water to cities like Los Angeles, Phoenix, and Tucson, and a canal carries water to California's Imperial Valley for crop irrigation. The salinity of the Colorado River (Table 2.1) increases significantly from the headwaters to the outlet in the Gulf of California. In fact, the United States withdraws so much water that the country operates desalination plants to resupply the river before it enters Mexico.

Table 2.2 shows analyses of several rivers in North America. These rivers contain generally soft to moderately hard water with low total dissolved solids (TDS). The two analyses of the Missouri River show that the dissolved and suspended solids increase from the headwaters in Montana to Kansas City.

European Rivers

Western civilization and culture developed along surface waters in Europe. Capital cities developed along rivers and streams, such as Rome along the Tiber River in Italy, becoming centers of commerce and transportation. Rivers became strategic borders between countries and empires. Many of these rivers are major shipping routes for several countries.

Location	Distance from Headwater, mi (km)	TDS mg/L
Near Grand Lake, CO	0	50
Hot Sulfur Springs, CO	30 (48)	150
Glenwood Springs, CO	140 (225)	460
Cisco, UT	320 (515)	710
Lees Ferry, AZ	610 (982)	520
Below Hoover Dam, AZ-CA Border	1000 (1610)	600
Above Morelos Dam, U.S.-Mexico Border	1330 (2140)	800

Source: USGS Scientific Investigations Report 2006-5315, 2007.

Table 2.1 Increase of Total Dissolved Solids (TDS) in the Colorado River from the Origin to the Border between the United States and Mexico, Near Yuma AZ

Several of the largest reservoirs in the world can be found along the Volga River. It is the largest and most voluminous river in Europe, with the largest watershed area. Many industries are found in the upper regions of the Rhine but most are concentrated along the lower Rhine. The river then turns west and enters the Netherlands, where it combines with other rivers to form one of the most extensive river deltas in Europe. One-fifth of the world's chemical industries are now manufacturing along the Rhine.[3] High levels of chemical pollutants are currently causes of concern for environmentalists in both rivers. Analyses of common inorganic ions in some of these rivers are shown in Table 2.3.

Other Great Rivers of the World

The Amazon River system is the greatest on earth, not even counting all of the tributaries (Fig. 2.3). Of these tributaries, 17 are over 1000 mi (1600 km) long, starting in Peru and flowing across Brazil to the Atlantic, where the Amazon is 4 to 6 mi (6–10 km) wide. The Amazon alone produces approximately 20% of all the water that the world's rivers empty into the oceans. Other great rivers are found in Egypt, China, and India.

These rivers have characteristics similar to the rivers in North America and Europe. However, rivers originating in equatorial rainforests, like the Amazon and the Orinoco in Venezuela, can be very low in dissolved solids but high in organics, especially near the headwaters (Table 2.4). Some portions of the immense Orinoco basin of Venezuela, a water-rich jungle, were never submerged beneath

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[3] Mutton, A., Sinnhuber, K., *Rhine River*, Encyclopedia Britannica, Aug 2016, https://www.britannica.com/place/Rhine-River.

Constituent	Calcium	Magnesium	Sodium	Bicarbonate	Carbonate	Sulfate	Chloride	Turbidity	TDS	Color	pH
Reported as	mg/L $CaCO_3$	mg/L $CaCO_3$	mg/L $CaCO_3$	mg/L $CaCO_3$	mg/L $CaCO_3$	mg/L $CaCO_3$	mg/L $CaCO_3$	NTU	mg/L	APHA units	pH units
Saskatchewan, Canada	107	54	12	110	10	48	4	5	208	13	8.4
Delaware at Morrisville, PA	23	19	4	10	0	35	10	NR	84	7	7.1
Chattahoochee at Atlanta, GA	9	4	5	12	0	2	3	26	33	4	6.9
Ohio at Steubenville, OH	57	30	14	13	0	79	8	88	143	2	6.4
Tennessee at Decatur, AL	58	20	18	55	0	15	21	50	113	30	5.6
Mississippi at St. Louis, MO	125	57	66	128	0	93	23	NR	326	19	7.9
Missouri at Great Falls, MT	100	49	47	140	0	36	16	150	234	NR	8.4
Missouri at Kansas City, MO	152	70	86	158	TR	120	27	2000	365	NR	8.3
Colorado at Los Angeles Aqueduct	198	105	220	113	7	302	100	NR	661	NR	8.4
Columbia at Wenatchee, WA	50	16	25	60	0	22	2	3	100	NR	7.7

These analyses represent a single point in time and location. (APHA = American Public Health Association, NR = not reported, NTU = nephelometric turbidity units, Tr = trace.)

Source: Nalco Water Analytical Water Analysis.

TABLE 2.2 Analyses of Selected North American Rivers

Constituent	**Calcium**	**Magnesium**	**Sodium**	**Bicarbonate**	**Carbonate**	**Sulfate**	**Chloride**	**Turbidity**	**TDS**	**Color**	**pH**
Reported as	**mg/L $CaCO_3$**	**mg/L $CaCO_3$**	**mg/L $CaCO_3$**	**mg/L $CaCO_3$**	**mg/L $CaCO_3$**	**mg/L $CaCO_3$**	**mg/L $CaCO_3$**	**NTU**	**mg/L**	**APHA units**	**pH units**
Danube	135	37	64	136	0	69	44	NR	250	NR	8.2
Tiber (Rome)	275	130	105	285	0	80	140	NR	575	NR	7.1
Po (Moncalieri)	159	66	37	182	0	58	20	21	270	NR	7.6
Seine (100 km below Paris)	244	60	43	154	0	100	95	NR	526	NR	6.9
Ebro (NE Spain)	350	110	333	180	0	290	323	NR	NR	NR	7.6
Severn	136	45	30	71	0	70	68	NR	NR	17	7.7

These analyses represent a single point in time and location. (APHA = American Public Health Association, NR = not reported, NTU = nephelometric turbidity units, Tr = trace.)

Source: Nalco Water Analytical Water Analysis.

Table 2.3 Analyses of Selected European Rivers

Figure 2.3 Amazon drainage basin in South America. (*Courtesy of NASA, Source: http://earthobservatory.nasa.gov/Study/AmazonLAI/.*)

prehistoric seas and therefore have had no contact with limestone. The dissolution of limestone makes water alkaline. The Orinoco and tributary rivers, like the Coroni, contact chiefly siliceous rock, such as flint, quartz, and sandstone. Decaying vegetation produces humic acid, and in the absence of alkalinity from limestone, the acidity of soils and rivers creates an environment hostile to humans and the kinds of plants and animals we depend on for sustenance. The Coroni River analysis in Table 2.4 illustrates that rivers flowing through drainage basins having dense vegetation and substantial rainfall are generally highly colored. In Venezuela and Brazil, the mineral content of the highly colored Coroni and Amazon Rivers is limited by the nature of the lithosphere and the heavy rainfall, especially the absence of limestone.

Surface Water—Lakes

Lakes are a major source of freshwater. The majority of lakes are in the Northern Hemisphere, mostly in the temperate regions. Over half of the world's lakes are in Canada. The ancient glaciers left an irregular land surface that held water as glaciers melted and this forms the basins of many of the lakes found in Canada. The Great Lakes in North America are usually considered the largest freshwater supply

Constituent	Calcium	Magnesium	Sodium	Bicarbonate	Carbonate	Sulfate	Chloride	Turbidity	TDS	Color	pH
Reported as	**mg/L $CaCO_3$**	**mg/L $CaCO_3$**	**mg/L $CaCO_3$**	**mg/L $CaCO_3$**	**mg/L $CaCO_3$**	**mg/L $CaCO_3$**	**mg/L $CaCO_3$**	**NTU**	**mg/L**	**APHA units**	**pH units**
Amazon (Brazil)	5	1	13	8	0	5	6	3–4	28	60–70	6.5
Coroni (Venezuela)	2	1	2	3	0	<1	3	30	NR	100	5.8
Nile (Egypt)	68	44	61	112	24	10	25	30	210	NR	8.5
Vaal (South Africa)	104	40	70	102	0	67	45	15	278	2	8.0
Orange (South Africa)	68	26	44	66	0	42	30	10	200	Tr	7.4

These analyses represent a single point in time and location. (APHA = American Public Health Association, NR = not reported, NTU = nephelometric turbidity units, Tr = trace.)

Source: Nalco Water Analytical Water Analysis.

TABLE 2.4 Analyses of Other Great Rivers of the World in the world. Lake Baikal in Siberia (Russia) is the largest freshwater lake by volume, containing as much freshwater as the entire Great Lakes system [5700 mi^3 (23 800 km^3)]. Lake Baikal is the deepest lake at about 5371 ft (1637 m) deep, with a surface area of about 12 200 mi^2 (31 500 km^2), compared with 95 000 mi^2 (246 000 km^2) for the five Great Lakes combined. Together, the Great Lakes and Lake Baikal contain 40% of the world's presently available fresh surface water. North America has countless smaller lakes, holding another 15% of the presently available freshwater of the world. Lake Victoria between Uganda, Kenya, and Tanzania and Lake Tanganyika bordering Tanzania are two of the great lakes of Africa.

North American Lakes

There are many lakes and reservoirs throughout the North American continent. The Great Lakes are a chain of five freshwater lakes located on the border between Canada and the United States (Fig. 2.4). They form the largest group of freshwater lakes on earth. Combined, they contain 5500 mi^3 (23 000 km^3) of freshwater by volume. Of the Great Lakes, Lake Superior is the largest, and the largest lake in the world by surface area [32 000 mi^2 (82 900 km^2)] with a maximum depth of approximately 1300 ft (400 m). It is also "the different lake," with significantly lower dissolved solids content than the other Great Lakes due to differences in geologic formations of the lakebed and the temperature (Table 2.5). Lake Michigan and Lake Huron have the largest area connecting the two lakes and are similar in chemical composition. The concentration of dissolved minerals is uniform, including the upper waters of the St. Lawrence River.

Great Lakes of Africa

The African continent has several large lakes, all near the Great Rift Valley in east-central Africa around Tanzania. Generally, Lake Victoria, Lake Tanganyika, Lake Nyasa, Lake Tukana, Lake Albert, and Lake Kivu are considered the main group, although there are several other large lakes in the same area. Lake Victoria and Lake Albert empty into the White Nile, the starting point of the Nile River. Lake Tanganyika and Lake Kivu empty into the Congo River. Lake Victoria is the world's second largest lake in terms of surface area, and Lake Tanganyika is the second largest by volume. Lake Tanganyika is also the world's longest lake, at 410 mi (660 km).

Salt Water Lakes

Some lakes in various parts of the world are saline lakes, some having salt content much higher than the oceans. They are generally remnants of ancient inland seas or were once connected to the oceans, but have been separated by the action of plate tectonics. Examples include the Caspian Sea in central Asia, the Great Salt Lake in the western United States, and the Dead Sea in the Middle East, all of which have no outlet.

Figure 2.4 The Great Lakes and their drainage basin. (*Courtesy of U.S. Army Corps of Engineers, Detroit District*.)

Constituent	Reported as	Lake Superior Duluth, MN	Lake Michigan Chicago, IL	Lake Huron Port Huron, MI	Lake Erie Erie, PA	Lake Ontario Cape Vincent, NY
Calcium	mg/L $CaCO_3$	35	90	90	90	91
Magnesium	mg/L $CaCO_3$	9	45	32	33	31
Sodium	mg/L $CaCO_3$	6	19	90	20	37
Bicarbonate	mg/L $CaCO_3$	42	113	71	91	90
Carbonate	mg/L $CaCO_3$	0	0	0	0	0
Sulfate	mg/L $CaCO_3$	1	18	35	25	25
Chloride	mg/L $CaCO_3$	5	9	37	27	27
Turbidity	NTU	1	12	NR	Tr	NR
TDS	mg/L	54	171	185	172	271
Color	APHA units	1	3	NR	2	NR
pH	pH units	7.4	7.8	8.1	7.5	8.2

Note that lake superior is much lower in TDS than the other lakes. These analyses represent a single point in time and location. (APHA = American Public Health Association, NR = not reported, NTU = nephelometric turbidity units, Tr = trace.)

Source: Nalco Water Analytical Water Analysis.

TABLE 2.5 Water Chemistry of Some of the Great Lakes in North America

The Caspian Sea has the largest surface area of any lake on earth, at 143 200 mi^2 (371 000 km^2) and a volume of 18 800 mi^3 (78 360 km^3). It has no outflow and is fed by many rivers, the largest being the Volga River. It has a maximum depth of 3360 ft (1024 m) and salinity of 1.2%, which is about a third of the salinity of seawater. The northern end of the lake is almost freshwater because of the influx of river water at this end.

The Great Salt Lake in northern Utah in the western United States is the largest saline lake in the western hemisphere. The size of the lake varies significantly because of periodic droughts and its shallow depth. It has variable salinity levels of 5 to 27%, much higher than the oceans of the world. The ratio of ionic components is similar to seawater, even though the ionic concentrations are much higher. The salinity of the water is maintained because of the geology of the Bonneville Salt Flats, where this lake is located, and also, like the Caspian Sea, the lake has no outlet. The lake is a source of salt, produced by solar evaporation ponds on the shore.

The Dead Sea is notable because it is the lowest point on the surface of the earth at about 1380 ft (420 m) below sea level. It is also the deepest hypersaline lake at 1080 ft (330 m). The salinity is approximately 30%, but its composition is very different from the oceans. The ionic content of most oceans and open seas is about 97% sodium chloride. The main ionic salts in the Dead Sea are magnesium chloride 51%, sodium chloride 30%, calcium chloride 14%, and potassium chloride 4%. Another unique feature of highly saline lakes, like the Dead Sea and the Great Salt Lake, is the extreme buoyancy they provide to swimmers; it is nearly impossible to sink in either of these lakes.

Circulation and Seasonal Turnover in Lakes

Lakes can be classified using a variety of characteristics. Looking first at latitude, lakes are broken into three categories:

1. Polar lakes
2. Temperate lakes
3. Tropical lakes

Elevation plays a role in the classification of lakes. The elevation of a lake above sea level can influence its characteristics, such that Alpine lakes can fall into either the temperate lake or the polar lake classification regardless of latitude. Lakes are further classified by the thermal properties of the water and the influence this has on how often the water in the lake mixes from top to bottom.

Temperate Zone Lakes There can be three distinct temperature zones or layers in a lake, particularly in regions where seasonal weather changes occur. These zones are called the epilimnion, metalimnion,

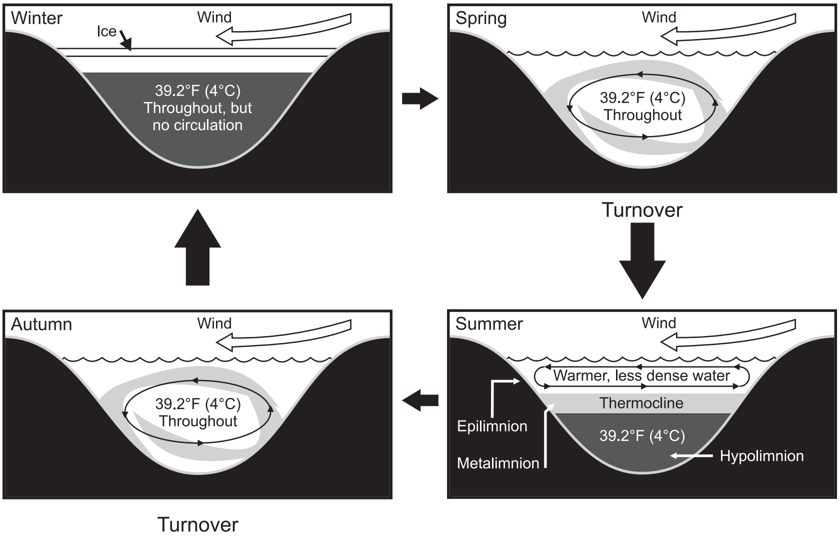

Figure 2.5 Temperature zones and seasonal turnover in temperate zone lakes.

and the hypolimnion (Fig. 2.5). The epilimnion is the water layer at the surface of the lake. This water is warmed by the sun, is subject to mixing by wind, and is usually well oxygenated. The surface layer, by virtue of its warm temperature, is the least dense water in the lake. The metalimnion is the middle layer in a lake, where the water temperature goes through a steep drop from warmer temperatures at the top of the metalimnion to cold temperatures at its bottom. The metalimnion is also called the thermocline because of the steep temperature drop in this layer. The hypolimnion is the water at the bottom of the lake. It is the densest and coldest water, generally at 39.2°F (4°C).

Depending on the depth of the lake, surface layer temperature, and season of the year, these layers can be stratified such that mixing of the different layers does not occur. Lakes that have shallow basins [<25 ft (7.6 m)] tend not to thermally stratify. Vertical circulation in shallow lakes is caused almost exclusively by wind action, since thermal density differences do not exist. Lakes with basins deeper than 25 ft (7.6 m) have the opportunity to thermally stratify into all three zones: the epilimnion, the metalimnion, and the hypolimnion. In these deeper lakes, the bottom layer is at or near the maximum density of water at a temperature of 39.2°F (4°C). In lakes with 25 to 200 ft (7.6–61 m) depth, the bottom temperature can vary slightly. In lakes over 200 ft (61 m) deep, the bottom temperature is at the temperature of maximum density all year round.

Thermal stratification occurs in summer, when the epilimnion of the lake warms and the surface water becomes less dense (Fig. 2.5). The ensuing density gradient prevents mixing of the water in the lake from top to bottom. The water mixes by wind currents in the epilimnion only. As the lake cools in the fall, the temperature of the epilimnion falls, and the water density increases. When the surface temperature reaches 39.2°F (4°C) and the density is the same from top to bottom, mixing can occur. Mixing or turnover of lake water is then a function of temperature and wind. There are other factors such as surface area, depth, topography around the lake, etc. that may inhibit complete mixing of the water. These only come into play once the thermal stratification of a lake is negligible and the lake does not have a density difference to overcome. When a lake turns over, the water may mix thoroughly from top to bottom. This action brings oxygenated water from the surface of the lake to the bottom and nutrient rich water from the bottom of the lake to the top. If the lake bottom is polluted, turnover can bring these contaminants to the surface.

When the lake freezes in winter, the water temperature and density can be the same in all water layers, or the water near the surface can be near 32°F (0°C), where it is less dense than the bottom water at 39.2°F (4°C). In either case, mixing does not occur because wind action is prevented by ice, or the lower density at the surface prevents mixing. In the spring when the ice melts, the water density is again similar from top to bottom and wind-driven mixing can occur. The cycle is repeated as the surface layer warms as spring transitions to summer.

An understanding of these characteristics of lakes is necessary to properly locate water intakes and discharges. It aids in anticipating the changes in water treatment needed to meet changes in composition caused by turnover and wind-induced circulation.

Tropical Zone Lakes Tropical lakes may have irregular mixing of surface and deep water or may be very stagnant. If mixing occurs, it is usually sporadic and occurs over a short time. Climatic conditions favor prolonged stratification of lakes in both the tropics and subtropics. Subtropical lakes may have more opportunity for a single turnover episode, because these areas have slightly more seasonal temperature variation than the tropics. The generally high air temperatures and lack of extreme seasonal fluctuations prevent water temperature and density changes in tropical zone lakes. This is because these lakes are typically warm from top to bottom, and once stratification is established, the density difference reduces opportunity for mixing of the water. In addition, the volume of the epilimnion is very large, and the air temperature would have to be low for a long time to make a significant temperature drop in this large surface layer. Rarely would cooling of the surface provide sufficient driving force for mixing. As a result, the bottom layer of water in many tropical lakes, particularly the deeper lakes, is permanently anoxic.

Groundwater

Underground reservoirs constitute a major source of freshwater. In terms of storage capacity, underground aquifers worldwide contain over 90% of the total freshwater available for human use. Much of this is too deep to be exploited economically, although new technology is increasing drilling capability. There are many different aquifers throughout the world. Figure 2.6 shows various aquifers in the United States. Over 76 billion gal/day (3,330 m^3/s) freshwater is withdrawn from wells for all uses in the U.S. mainland.[4] Approximately one-third of this well water is used by municipalities throughout the United States, and the other two-thirds are used for irrigation and industrial purposes. Over 80% of the municipalities in the United States depend on well water, although less than 30% of the total volume of water treated for municipal use is from this source. Industry draws approximately 14 billion gal/day (613 m^3/s) from wells. The state of California withdraws the freshest groundwater for industrial use, accounting for 14% of the total national groundwater industrial withdrawals.

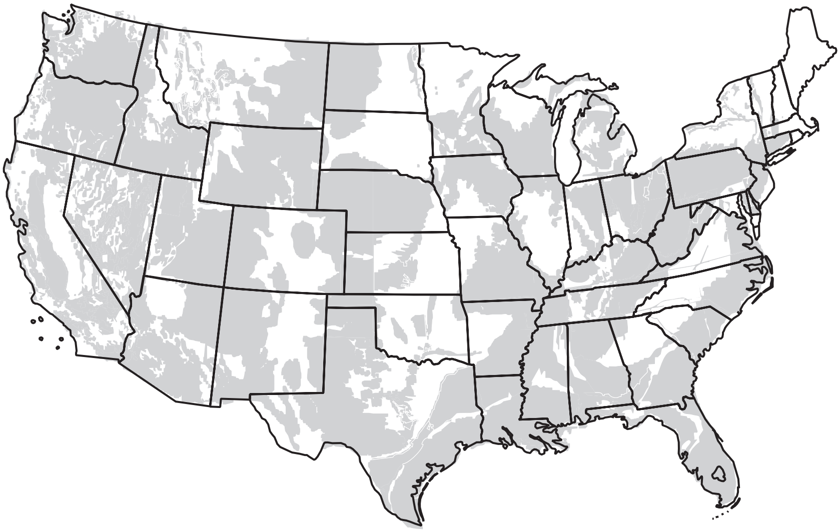

FIGURE 2.6 Illustration of the many different aquifers in the U.S. mainland. (*Courtesy of the U.S. Geological Survey, Source: nationalatlas.gov.*)

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[4] USGS, *Estimated Use of Water in the United States in 2010*, U.S. Geological Society, Circular 1405, http://pubs.usgs.gov/circ/1405/.

Connate Water

The term connate water refers to water that is trapped inside sedimentary rock as the rock formation deposited and solidified. The water is often dense and saline and can change composition over the course of time in a formation. Connate water is generally released with the production of oil and often called oilfield brine. The brine creates unusual problems for handling and treatment for reuse or disposal. It is usually more concentrated than seawater, sometimes exceeding 100 000 mg/L in total salinity. The high mineral content and the reduction in temperature and pressure as the brine travels upward from great depths cause difficult problems for scale and corrosion control. Several analyses are shown in Table 2.6.

Desalination

With all that salt water in the world, one would think desalination plants would be a significant part of the water treatment landscape. Presently, the amount of capacity to generate freshwater by desalination makes up less than 1% of total world freshwater use.[5] Installed desalination capacity on a global basis has continued to rise each year from the late 1960s to present. Cost for desalination continues to remain higher than water use from existing freshwater sources, freshwater reclaim, or freshwater cleanup, but it is coming down. More than 76% of the installed desalination capacity is in the Persian Gulf, Middle East, and North Africa. As these parts of the world are generally considered in a water stressed or water scarce environment, it is no surprise that desalination would be occurring more here than in other parts of the world.

Evaporators

Creating freshwater from seawater using thermal distillation or multi-effect evaporators mimics the earth's natural hydrologic cycle. Pure water is evaporated, captured, and then condensed (Fig. 2.7). The resulting waste stream discharge is of much higher salinity and temperature due to the thermal process of evaporation. These types of plants were used in the early days of desalination and still represent about 40% of installed capacity. They are energy intensive with roughly 60% of the cost to generate freshwater coming from either thermal or electrical energy. As energy costs continue to rise, the costs to produce freshwater also continue to rise in these types of plants.

Reverse Osmosis

Use of membranes for desalination began in the 1970s. As the cost of membranes continues to come down, the use of reverse osmosis (RO)

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[5] USGS, *Estimated Use of Water in the United States in 2010*, U.S. Geological Society, Circular 1405, http://pubs.usgs.gov/circ/1405/.

Constituent	Reported as	Sample 1	Sample 2	Sample 3	Sample 4
Calcium	mg/L Ca	8300	2630	1500	630
Magnesium	mg/L Mg	260	690	500	40
Sodium	mg/L Na	56 250	16 800	9150	5640
Bicarbonate	mg/L HCO_3	50	315	1000	500
Sulfate	mg/L SO_4	180	2880	2000	120
Chloride	mg/L Cl	98 300	30 550	17 800	8350
TDS	mg/L	166 650	54 070	32 330	15 420

Table 2.6 Four Different Connate Waters Illustrating the High Dissolved Solids, Mostly Sodium and Chloride (*Source: Nalco Water Analytical Water Analysis*.)

Figure 2.7 Multi-stage flash desalination plant at Jebel Ali G Station, Dubai (*CC BY-SA 3.0, via Wikimedia Commons*.)

systems for desalination continues to increase. Virtually all of the brackish water desalination is now accomplished by membrane separation, and a good portion of seawater is now being processed through membranes. These are less energy intensive, with 30 to 40% of the operational cost attributed to electrical energy.[6] RO desalination has the additional benefit of minimal thermal impact on the environment (Fig. 2.8). Several thousand desalination facilities are in operation worldwide, many in the Middle East.

Recycled Wastewater

Reuse of municipal discharge by industry is no longer a rarity; each instance presents unique problems, but the need for water in arid places has given economic incentive to practical solutions. In the United States, reuse of domestic discharge as barrier water, as described earlier, is the only example where a small flow of treated sewage may eventually return to potable wells. In South Africa, where the total amount of available water is only 20 billion gal/day (876 m^3/s), with 60% being used for irrigation and 40% for all other uses, research has been conducted on direct return of a portion of highly treated discharge to municipal water plant intakes.[7] The city of Windhoek in Namibia has practiced such recycle for over a decade,

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[6] Water Reuse Association, *Seawater Desalination Costs, White Paper*, Water Reuse Desalination Committee, Jan 2012, https://watereuse.org/wp-content/uploads/2015/10/WateReuse_Desal_Cost_White_Paper.pdf.

[7] FAO, *South Africa—Geography, climate and population*, Food and Agriculture Organization of the United Nations, 2016, http://www.fao.org/nr/water/aquastat/countries_regions/zaf/index.stm.

Figure 2.8 Reverse osmosis bank producing freshwater from seawater. (*Courtesy of Water Services of America and Dupont*.)

producing drinking water for nearly 300 000 people.[8] This may become a growing practice as South Africa works to offset a 5% deficit in natural water supplies that began in the year 2000.

Fairfax County in Virginia began recycling wastewater in 1978 into the Occoquan Reservoir, which is the drinking water supply.[9] Municipalities that discharge treated discharge into rivers, upstream of other cities, inadvertently engage in recycling of water. Many other cities and municipal districts directly participate in this growing trend to recycle wastewater. In January 2008, Orange County in California started a new advanced treatment plant to recycle sewage effluent into drinking water. The facility can produce 100 million gal/day (3 m^3/s), enough to meet the needs of nearly 850 000 residents. The treatment plant takes secondary treated sewage, which is disinfected and sent through microfiltration and reverse osmosis. The final step is advanced oxidation by hydrogen peroxide and ultraviolet light. The water is reapplied to the aquifer in two ways. One-third of the water is sent to reinjection wells near the coast to prevent seawater intrusion. The other two-thirds of the water is pumped to two retention basins

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[8] Veolia, WINGOC: *Wastewater to clean water—Windhoek, Namibia*, http://www.veolia.com/africa/our-services/achievements/municipalities/veolia-optimized-resource-management/wingoc-wastewater-clean-water-windhoek-namibia.

[9] Upper Occoquan Service Authority, http://www.uosa.org.

over permeable soil, where the water percolates into the ground to replenish the aquifer.[10]

Stress on Water Sources

As noted earlier, the United Nations defines water stress as a population with a water supply that drops below 449 000 gal (1700 m^3) per person per year. At present, roughly 40% of the world's population lives in an area that can be described as under water stress. This number is expected to reach more than 47% by the year 2030.

Groundwater Stress

Groundwater over-pumping is resulting in a lowering of water tables in aquifers from which water is drawn. In many parts of the world, water is being removed from the ground faster than it is being replenished by rainfall and snowfall. While the removal rate is a significant portion of the problem, the recharge rate is equally important. As more of our land is converted to urban use, controlled urban runoff is directed to surface waterways, and the natural seepage of water into the ground to replenish groundwater does not occur. Extracted water in these cases is essentially being mined. Wells then need to reach deeper into the ground in order to tap water resources. Many areas of the Middle East, China, India, and North Africa are experiencing significant drops in the water table. Even in parts of Mexico wells have had to be deepened to maintain adequate water flow. The additional cost of deep water wells not only upsets food production costs, but increases domestic and industrial use costs as well. The cost of water is increasing. In some parts of the world, it is increasing to the point of making certain agricultural practices and crop mixes no longer economical.

Groundwater is mined extensively in many areas of the United States, particularly the west and south. In fact, California, Texas, and Florida account for 30% of the groundwater usage in the United States.[11] This removal has resulted in net loss of water, which can reduce the level of water in an aquifer by as much as 100 ft (30 m). Figure 2.9 shows the High Plains Aquifer (also called the Ogallala Aquifer) in the central United States and the changes in water level of this aquifer from predevelopment to 2013.[12] This aquifer, one of the

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[10] Orange County Water District, *GWRS—new water you can count on*, http://www.ocwd.com/gwrs/.

[11] USGS, *Estimated Use of Water in the United States in 2010*, U.S. Geological Survey, Circular 1405, http://pubs.usgs.gov/circ/1405/.

[12] USGS, *Water-Level Changes and Change in Water in Storage in the High Plains Aquifer, Predevelopment to 2013 and 2011–13*, U.S. Geological Survey, Scientific Investigations Report 2014–5218, 2014, https://pubs.usgs.gov/sir/2014/5218/pdf/sir2014_5218.pdf.

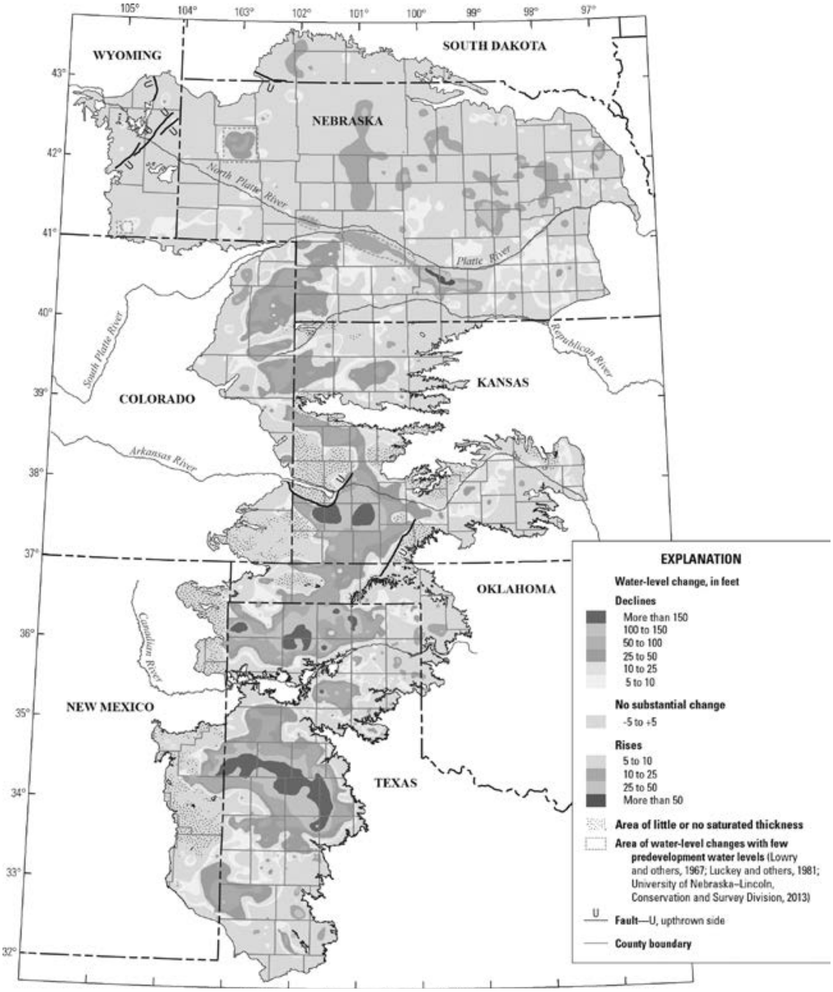

Figure 2.9 Area covered by the High Plains Aquifer (Ogallala Aquifer) and changes in water table level predevelopment to 2013. Note that more areas have lost water than gained. (*Courtesy of the U.S. Geological Survey, Source: USGS Scientific Investigations Report 2014-5218*.)

largest in North America, lies under about 175 000 mi^2 (451 000 km^2) of land in portions of eight states. In 2005, the amount of irrigated acreage overlaying the aquifer area totaled about 14%. Water-level declines began around 1950 as substantial groundwater pumping for irrigation began. By 1980, some parts of the aquifer in Texas, Oklahoma, and southwestern Kansas were experiencing a decline of more than 100 feet.[13]

In coastal areas, pressure on the groundwater supply due to increased domestic, agricultural, and industrial use opens up the opportunity for saltwater contamination of freshwater aquifers, turning the water brackish. Should this occur, groundwater in that location can become impaired or even unsuitable for use, depending upon the degree of contamination by saltwater. This situation is a particular problem for island nations in the Pacific and Caribbean, where saltwater intrusion to freshwater wells occurs increasingly further inland.[14]

In other areas, steady reduction of the water table has contributed to land subsidence. Beijing, China, has been experiencing land subsidence since 1935 due to over exploitation of groundwater. While some areas of Beijing have had little impact, eastern Beijing has seen a displacement rate greater than 100 mm/year.[15] In some areas of the United States, such as near Great Neck, New York on Long Island, heavy withdrawal, continuous sea rise and drought conditions drying up streams and lakes have resulted in land subsidence and intrusion of seawater into the aquifer.[16] Caps have been placed on the amount of water that can be pumped to limit further contamination.

Augmentation

Augmentation of a groundwater source by artificial recharge has also been practiced, where a nearby source of surface water has been available for this purpose. The aquifer becomes, in effect, a storage reservoir. The city of Los Angeles reclaims storm water and segregated wastewater of selected quality, by gravity recharge of underground reservoirs using the Los Angeles River.[17] The natural

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[13] USGS, *Saturated Thickness and Water Storage in the High Plains Aquifer, 2009, and Water-Level Changes and Changes in Water Storage in the High Plains Aquifer, 1980 to 1995, 1995 to 2000, 2000 to 2005, and 2005 to 2009*, U.S. Geological Survey, Scientific Investigations Report 2012–5177, 2012, http://pubs.usgs.gov/sir/2012/5177/sir12-5177.pdf.

[14] Berthe, L., Change Seng, D., Lameko, A., *Multiple Stresses, Veiled Threat: Saltwater Intrusion in Samoa*, National University of Samoa, Apia, Samoa, Aug 2014, http://samoanstudies.ws/wp-content/uploads/2015/03/Leo-Berthe-Dennis-Chang-Seng-and-Lameko-Asora.pdf.

[15] Chen, M. et al, Imaging Land Subsidence Induced by Groundwater Extraction in Beijing (China) Using Satellite Radar Interferometry, Remote Sensing, Vol. 8, Issue 6, 2016, http://www.mdpi.com/2072-4292/8/6/468/htm.

[16] ESERC, *Long Island Groundwater*, Earth Science Education Recourse Center, http://www.eserc.stonybrook.edu/cen514/info/LI/Groundwater.pdf.

[17] SWRCB-CA, *Los Angeles River Watershed*, State Water Resources Control Board—California, http://www.waterboards.ca.gov/rwqcb4/water_issues/programs/regional_program/Water_Quality_and_Watersheds/los_angeles_river_watershed/la_summary.shtml.

riverbed has been paved with concrete to prevent haphazard loss of collected water to the ground, and a collapsible dam has been constructed at the river's end. Collected waters are spread over the old, natural river delta for percolation through the original gravel riverbed into the underground reservoirs. During a heavy storm, the dam is momentarily and deliberately collapsed to flush out collected solids, then reinflated. This arrangement provides for recovery of most of the storm water in this arid metropolis.

Surface Water Stress

Surface water stress occurs in both quantity and quality of available water. Around the world, several major rivers no longer maintain significant flow at their former deltas. Examples are the Colorado, Ganges, Huang He, Jordan, Nile, and Rio Grande rivers. Competition for water upstream of the delta in the form of hydroelectric dams, crop irrigation, and domestic and industrial use have all taken their tolls on these rivers, and they now regularly run dry before they reach their deltas. By far, the biggest culprit here is water extraction for irrigation. The more water that is removed upstream, the less is available downstream for other consumption.

Agricultural irrigation practices around the world at present only return about 30% of extracted water back to either surface waterways or groundwater; the balance of extracted water is either consumed or lost.[18] While hydroelectric dams do not extract water, they do control the flow of water, exacerbating effects of water extraction downstream of dams. Reduced flow at the delta affects wetlands and water quality, as brackish water pushes further into the delta.

While industrial and domestic water users do return the majority of water back to the environment, the quality of the returned water in many parts of the world is significantly lower than that of the original extraction. This lowering of water quality becomes an issue when discharge back to surface waterways such as lakes and rivers contains industrial pollutants and sewage, which make water unsuitable for human consumption. Up to 12% of the world's population does not have a regular source of clean water for domestic use.[19]

As mentioned, upstream practices affect downstream quantity and quality. As pressure increases on our river systems, we see the effects at the discharge of rivers to either inland bodies of water or estuaries, where rivers reach the seas. Take, for example, the Dead Sea. In the past 70 years, the drainage basin of the Dead Sea has seen increased extraction of water and damming of influent rivers.

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[18] FAO, *Water Resource Issues and Agriculture*, Food and Agriculture Organization of the United Nations, http://www.fao.org/docrep/003/t0800e/t0800e0a.htm#TopOfPage.

[19] FAO, *Water Resource Issues and Agriculture*, Food and Agriculture Organization of the United Nations, http://www.fao.org/docrep/003/t0800e/t0800e0a.htm#TopOfPage.

The influent water volume has reduced by about 85%, and consequently, the Dead Sea has reduced in size. The water level of the Dead Sea has fallen by 20 m, and its surface area has been reduced by about one-third.[20]

The Aral Sea in Central Asia has been also experiencing significant water loss. In the 1950s, the Amu Darya and Syr Darya rivers that fed the Aral Sea were diverted to supply irrigation systems to support a new agrarian project. The water level in the sea began to fall in the 1960s. By the 1980s, indigenous fish species could no longer tolerate increasing salinity of the water, and they began to die. The fishing industry went into complete collapse. At present, the Aral Sea is now only 10% of its former volume, and the remnants are hyper-saline in nature.[21] In this case, it is not that there is not enough water in the Aral Sea basin to support the sea; it is the complete extraction of the water before reaching the sea that is causing the issues.

The Rio Grande River basin that empties into the Gulf of Mexico is another example of upstream over-extraction. The estuary at the delta of the Rio Grande River now only sees about 10 to 15% of historic water flow; the balance of the water is extracted upstream. This severe reduction in flow is resulting in an increased intrusion of seawater into the estuary, resulting in an increase in salinity of the estuary water.[22]

Now that we have taken inventory of the world's freshwater sources, we will drill deeper into the water chemistry or water quality of these various sources. Water quality is not only important for human use, but to every aspect of industry from food producers to oil refineries.

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[20] Hammer, J., *The Dying of the Dead Sea*, Smithsonian Magazine, Oct 2005, http://www.smithsonianmag.com/science-nature/the-dying-of-the-dead-sea-70079351/?no-ist.

[21] Columbia University, *The Aral Sea Crisis*, http://www.columbia.edu/~tmt2120/introduction.htm.

[22] WWF Global, *Rio Grande: Threat of Water Extraction*, World Wildlife Fund, http://wwf.panda.org/about_our_earth/about_freshwater/freshwater_problems/river_decline/10_rivers_risk/rio_grande_bravo/riogrande_threats/.

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CHAPTER 3

Water Quality

Water quality of both surface and groundwater can be affected by many things. Natural forces such as rainfall, geological characteristics, and seasonal changes can have significant impact. Human activities, including overuse, pollution, changes in water flow patterns, introduction of non-native species, and dams on rivers can have unintended consequences. These factors can affect how water is treated and the results of water treatment.

Industrial water demands are ever changing, and with these demands come the need to continuously find ways to both improve the quality of water and extend its usefulness in operations. Many of our industries require water of very high purity for their production environment, such as semiconductor manufacturing, certain chemical processes, and pharmaceuticals. Other industries, such as power utilities, require higher purity water for makeup to high-pressure steam generating equipment. These increasing water quality requirements demand increasingly sophisticated equipment and chemistries to ensure the purity of water matches the specification for the industry or application.

In addition to the need for increasing water purity across industries and processes, we are increasingly faced with the need to stretch our use of existing plant waters, by managing the water chemistry before discharge, cascading to other process uses in a plant, or recycle and reuse of waste streams. This multiple use of the same water results in treatment needs to ensure the quality or characteristics of the water are appropriate for the next use.

Natural Factors Affecting Water Quality

The quality of surface waters is affected by rainfall, the geological nature of the watershed, conditions of evaporation, seasonal changes in stream flow, and location. The effect of rainfall on lakes and rivers obviously depends on the size of the body of water. For example, the headwaters of most rivers are more greatly affected by rainfall and other inputs when compared with points downstream, because the volume of river water flow is much greater downstream (greater dilution).

A key factor involved in increases in mineral content of water is the dissolution of mineral bearing rock. Calcium bearing rock is the most prominent of those readily soluble in water and is contained in limestone ($CaCO_3$), which is an alkaline compound. $CaCO_3$ comes from shells and skeletons of aquatic organisms in the bottom of prehistoric seas. The dissolution of minerals, as well as entrainment of soil as suspended solids in the catchment area, can affect the composition of lakes and rivers.

Well water composition is related to the chemistry of the geologic formations through which the water passes. Thus, waters from wells drilled into different strata have different characteristics. Underground water usually moves very slowly. Its flow is measured in feet per year (meters per year) compared with surface streams, where velocity is in the feet per second (meters per second) range. Because of this slow movement, the composition of any given well is usually quite constant. Although shallow wells may vary seasonally in temperature, most wells are constant in temperature, usually in the range of 50 to 60°F (10–15.6°C). Since the water often passes through miles of porous rock formation, well water is generally clear, if the well has been properly constructed to keep fine sand from entering the casing (Fig. 3.1).

Rainwater filtering through the ground picks up nutrients and minerals, depending on the composition of the soil and rock strata. From flowing streams and rivers, water may diffuse into underground aquifers when the surrounding water table is low; or water may feed into the river from these aquifers when the water table is high. This too influences chemical composition, particularly iron and manganese in certain streams. See Chap. 5 for more information on this process and the differences between surface and groundwater.

Some aquifers are so large that they may cover several states in total area, and wells drilled into that particular aquifer produce water of similar composition. For that reason, with good geological information, it is possible to generalize about the composition of well waters in different parts of the world. Selected analyses of North American wells are shown in Table 3.1. Most of the waters have

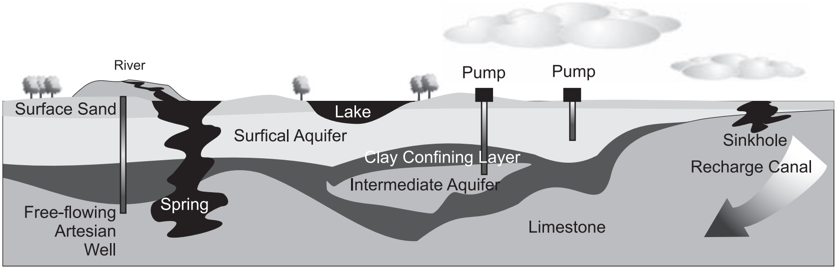

Figure 3.1 An aquifer system illustrating wells at various depths into the water table.

Constituent	Calcium	Magnesium	Sodium	Bicarbonate	Carbonate	Sulfate	Chloride	Turbidity	TDS	Color	pH
Reported as	mg/L $CaCO_3$	mg/L $CaCO_3$	mg/L $CaCO_3$	mg/L $CaCO_3$	mg/L $CaCO_3$	mg/L $CaCO_3$	mg/L $CaCO_3$	NTU	mg/L	APHA Units	pH Units
Ontario, Eastern Canada	180	80	22	210	0	41	21	0	300	5	7.5
Saskatchewan, Central Canada	352	232	750	380	0	307	670	2	1650	5	7.3
Camden, NJ, Eastern U.S.	42	41	31	91	0	12	10	NR	118	3	6.8
Ft. Lauderdale, FL, SE U.S.	230	8	22	235	0	TR	25	NR	315	59	7.7
Bastrop, LA, Southern U.S.	4	2	616	356	0	2	262	NR	697	35	8.0
Dallas, TX, Southern U.S.	15	9	838	452	TR	270	134	NR	1040	0	8.2
Norman, OK, Central U.S.	5	3	462	295	57	98	18	NR	550	5	9.1
Manhattan, KS, Central U.S.	282	86	65	352	0	54	25	NR	488	2	7.3
Phoenix, AZ, SW U.S.	192	230	319	220	0	128	312	NR	887	3	7.9
Richland, WA, NW U.S.	125	65	38	169	0	45	13	NR	307	5	7.7

Note the variation from very soft water to hard water. These analyses represent a single point in time and location. (APHA = American Public Health Association, NR = not reported, NTU = nephelometric turbidity units, Tr = trace.)

Source: Nalco Water Analytical Water Analysis.

TABLE 3.1 Analyses of Various Well Waters in North America calcium, magnesium, and alkalinity typical of wells in limestone-based formations. Some, like the well in Dallas, TX, may have passed through strata that are rich in sodium carbonate, chloride, and sulfate rather than calcium carbonate.

Often, the well waters of Mexico are high in silica, like well waters of the southwestern United States. Well waters of central Europe are like those of the U.S. Midwest and are as variable in quality based on location, the nature of the geologic formations, and depth. An analysis of an industrial well outside Vienna is shown in Table 3.2. A well-water analysis from a refinery on the Adriatic coast of Croatia is unusual in its low sulfate and chloride level, and a low ratio of magnesium to calcium. It is obvious from these and other analyses in this chapter that accurate prediction of a water analysis is not possible, and throughout the world, each source is unique.

Seasonal Changes That Affect Water Quality

The sudden dilution of a river by heavy rainfall can change the water quality significantly. This change can be a disruptive factor in a water pretreatment application that prepares water for either industrial or domestic use, such as clarification or lime softening. The location of a river water intake should be carefully chosen with this problem in mind. In the operation of a treatment plant, it is common practice to adjust the chemical dosages according to effluent water quality. However, when the water supply is so variable, it is necessary to base changes in chemical treatment on raw water characteristics, rather than on finished water quality. This imposes a hardship on treatment plant operators, requiring constant attention to analysis and control.

Seasonal temperature change is another characteristic of surface water that complicates treatment, particularly affecting the coagulation process and softening reactions in the winter. Low temperatures create problems with air binding of filters due to the increased solubility of gases and higher water viscosity. Air binding causes pressure drop through the filter beds to increase releasing gas and disrupting flow.

Seasonal water temperature change can cause problems in cooling water systems. The heat exchange equipment is usually designed for the least favorable condition, which is the higher summer temperature of surface waters. In winter, when the water temperature is low, the flow through heat exchangers must often be restricted to prevent overcooling. Lower water velocity may allow fouling in heat transfer equipment, which can lead to corrosion and lost heat transfer capacity. Generally, the lost heat transfer capacity cannot be recovered with higher flow rate when higher cooling rates are needed.

Impact of Dams on River Water Quality

When a river is dammed, the water quality may be considerably different from that of the flowing stream. The impoundment behind

Constituent	**Calcium**	**Magnesium**	**Sodium**	**Bicarbonate**	**Carbonate**	**Sulfate**	**Chloride**	**Turbidity**	**TDS**	**Color**	**pH**
Reported as	**mg/L $CaCO_3$**	**mg/L $CaCO_3$**	**mg/L $CaCO_3$**	**mg/L $CaCO_3$**	**mg/L $CaCO_3$**	**mg/L $CaCO_3$**	**mg/L $CaCO_3$**	**NTU**	**mg/L**	**APHA Units**	**pH Units**
Vienna, Austria	160	120	6	220	0	40	26	Tr	NR	NR	7.7
Rijeka, Croatia	136	27	39	180	0	10	12	Tr	NR	NR	7.5
Canary Islands	50	135	760	144	6	48	251	NR	NR	NR	8.4
Tarragona, Spain	557	672	1891	181	0	181	0	NR	NR	NR	7.9

These analyses represent a single point in time and location. (APHA = American Public Health Association, NR = not reported, NTU = nephelometric turbidity units, Tr = trace.)

Source: Nalco Water Analytical Water Analysis.

Table 3.2 Analyses of Selected Wells in Other Countries the dam takes on the characteristics of a lake. In deep impoundments, it is common to find stratification, with oxygen depletion in the bottom stagnant zone. Significant levels of iron and manganese can develop in the bottom water, even though the surface remains free of these metals. Concentration gradients are sometimes found in impounded lakes, indicated by an increase in conductivity with depth. For example, Lake Mead, the impoundment of the Colorado River above Hoover Dam on the Nevada-Arizona border, has a conductivity of 900 μS/cm at the surface. Conductivity begins to increase at a depth of 50 ft (15 m), reaching 1150 μS/cm at 300 ft (91 m). At the bottom, about 460 ft (140 m), the conductivity abruptly increases to almost 1500 μS/cm.

In the impoundment of major rivers, such as the Columbia, the Colorado, and those in the Tennessee Valley system, the mineral content of the lakes behind the dams is similar to that in the river, as would be expected. On the other hand, natural or artificial impoundment of streams in smaller watershed areas of abundant rainfall produces water supplies of very low mineral content. This accounts for the excellent quality of such municipal waters as Greenville, South Carolina, New York City, and Boston, as shown in Table 3.3.

Water Quality When River Meets Ocean

Rivers generally flow into oceans through either an estuary or a delta. An estuary is typically a wide mouth of a river open to the ocean. A delta is formed by the deposition of river sediment into another

Constituent	Reported as	Greenville, SC	New York, NY (Catskill Mt.)	Boston, MA
Calcium	mg/L $CaCO_3$	3	12	10
Magnesium	mg/L $CaCO_3$	2	7	3
Sodium	mg/L $CaCO_3$	4	4	1
Bicarbonate	mg/L $CaCO_3$	6	8	5
Carbonate	mg/L $CaCO_3$	0	0	0
Sulfate	mg/L $CaCO_3$	2	11	6
Chloride	mg/L $CaCO_3$	1	4	3
Turbidity	NTU	NR	2	1
TDS	mg/L	17	34	33
Color	APHA units	6	1	7
pH	pH units	6.2	6.9	6.3

Source: Nalco Water Analytical Water Analysis.

TABLE 3.3 Analyses of Reservoirs or Lakes Where Water Quality Is Impacted Mainly by Rainfall body of water, such as the ocean. Many of the major rivers of the world finally reach the ocean through deltas, which may have some of the characteristics of an estuary. In many instances, the flow of these rivers is so great that the dilution of the ocean can be measured for miles (kilometers) out to sea.

Power utilities in coastal areas often use brackish water for once-through cooling water. Some industrial plants have used the brackish waters of tidal basins for cooling tower makeup, since the water is low enough in dissolved solids to be concentrated by evaporation without severe scaling problems. The use of brackish water for this purpose permits installation of much smaller pipelines than would be needed if once-through cooling were practiced. One example is a chemical plant on the island of Trinidad, which is able to use water from the bay side of the island as cooling tower makeup. This water is diluted enough by the immense flow of the Orinoco River so that its salinity is lower than typical ocean water, permitting it to concentrate by evaporation without causing scale problems.

The quality of water in estuaries where rivers meet the sea is unpredictable, depending on river flow, tidal conditions, the size of the basin or bay, and the presence or absence of land formations that restrict flow to the sea. In large basins, such as Albemarle Sound in North Carolina on the U.S. east coast, the water, although saline, is of relatively uniform composition because of mixing of the shallow water by wind; but in smaller bays, the quality can change with the tides and the flow of the river. It is one of the miracles of nature that aquatic life adapts to these changes and flourishes in such tidal areas.

Tides influence surface water quality in that they slow, or actually reverse, normal river flow. This is particularly pronounced during periods of low rainfall. The change in water quality between high and low tide sometimes justifies installation of raw water supply reservoirs to receive water at low tide, when the river flows unimpeded and quality is at its best. Plants so equipped stop pumping at high tide, when saline bay waters move upstream into the river channel. An example of the effect of tides and seasonal runoff is given in Table 3.4, showing the enormous variations in the Delaware River near Wilmington, Delaware.

Out at sea, where surface waters have become part of the circulation system, the composition of the ocean water is remarkably uniform. There are, of course, local changes in salinity, as mentioned earlier, caused by upwelling of subsurface waters into the ocean, the flow of mighty rivers into the sea, or the melting of glaciers and the polar ice caps. Even though it is not usable by land animals, seawater is a valuable source of water for industry and is widely used for cooling.

Pollution

Pollutants from domestic water discharge, industry, and agriculture can degrade surface water systems and seep through the ground

Date	Maximum	Minimum	Mean
October 16	6880	2660	4420
November 26	2460	420	1370
December 27	240	100	145
January 17	2700	100	1470
February 24	560	100	235
March 21	3240	200	1450
April 23	1240	220	289
May 24	4220	920	NR
June 22	3900	200	1110
July 20	6380	860	2930
August 19	8920	1900	5030
September 20	8300	3500	5630

Source: USGS Water Supply Paper 2151, 1970.

Table 3.4 Conductivity (μS/cm) of Delaware River Near Wilmington, DE from October 1969 to September 1970 Showing Daily Variations Due to Tidal Flow

causing contamination of aquifers. Reinjection of water to replenish aquifers can affect water quality and pollute groundwater, if the injected water is not of sufficient quality. Industrial discharges may lower pH and alkalinity or increase organic and biological contamination. Municipal water may show an increase in dissolved solids of 50 to 100 mg/L through human use. Pollution is a major concern for lakes and rivers around the globe. In many lakes, this consists of runoff from farms during rainstorms in which the major pollutant is fertilizer. Lakes in industrial areas can receive various chemical pollutants. Cities around larger lakes may actually dump raw sewage into lakes, when rainfall is heavy and the waste treatment systems become overloaded. As a result, there are wide varieties of pollutants that affect water quality.

The temperature of industrial cooling water discharge can be considered pollution. A large once-through cooling system can cause local temperature changes in a river or small lake. The added heat from plant processes, compounds the natural rise of the summer water temperature, sometimes producing an effluent warm enough to create an unhealthy condition for aquatic life. The higher temperature discharge can add to the oxygen demand and may have a pronounced influence on the oxygen content of the river water.

When pollutants are biodegradable, bacterial activity in surface water increases with pollution load, tending to reduce the dissolved oxygen level in the stream, but there are offsetting factors. The principal one is the presence of algae, which produce oxygen by photosynthesis in daylight often causing oxygen supersaturation on bright sunny days, followed by a concentration decrease at night as photosynthesis stops. This diurnal cycle affects not only dissolved oxygen, but also carbon dioxide, and thus pH. This can have a strong influence on the coagulation of a water supply in municipal and industrial water treatment plants.

Effects of Acidic Rainfall

The term “acid rain” commonly describes the deposition of acidic components in rain, snow, fog, dew, or dry particles. Distilled water, which contains no carbon dioxide, has a neutral pH of 7. Liquids with a pH less than 7 are acidic, and those with a pH greater than 7 are alkaline. Clean or unpolluted rain is slightly acidic with a pH of about 5.5. This is due to natural carbon dioxide in the air reacting with water to form carbonic acid.

Since the industrial revolution, emissions of sulfur dioxide and nitrogen oxides to the atmosphere have increased. They are discharged from utility stations, ore smelters, and internal combustion engines, including diesel locomotives, automobiles, and trucks. In general, the major contributor of nitrogen oxides is transportation, and the major contributor of sulfur oxides is the electric utility industry. The sulfur and nitrogen oxides react with water to form sulfurous, sulfuric, and nitric acids. These gases acidify the rain, sometimes to a pH of 2.4, downwind from industrial areas. The pH profile over the United States is shown in Fig. 3.2. Industrial acid rain is not only a problem

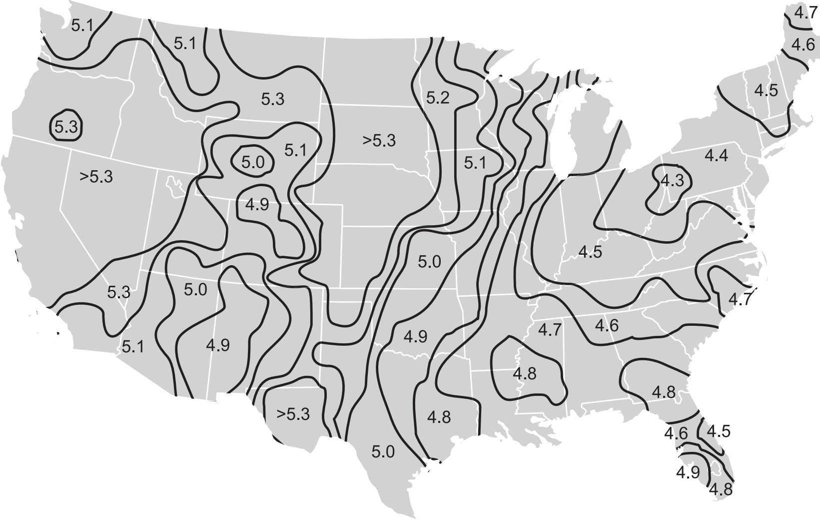

Figure 3.2 The pH of rainfall across the United States in 1997, showing the lower pH in the east due to acidic gases and prevailing winds. (*Compiled from information available through the National Atmospheric Deposition Program of the Illinois State Water Survey.*)

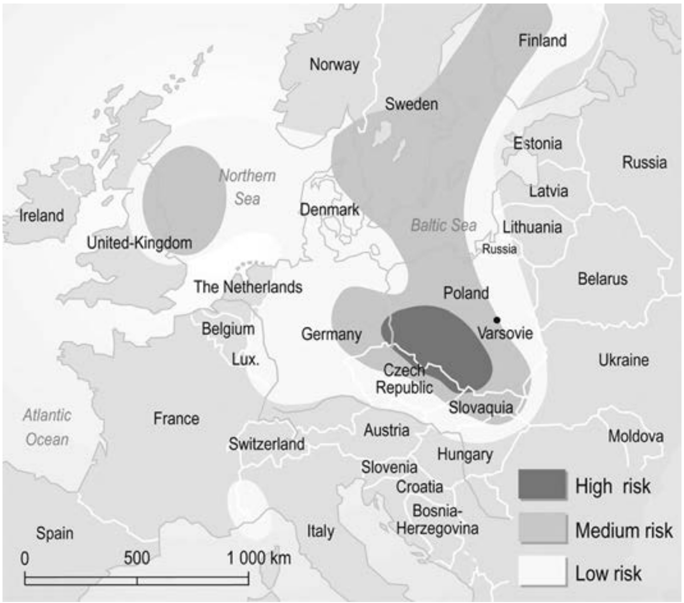

Figure 3.3 Areas across Western Europe susceptible to acidic rainfall. (*Source: Ed. Hatier, Paris, 1993, Cartographer: Philippe Rekacewicz, UNEP/GRID-Arendal, http://maps.grida.no/go/graphic/acid_rain_in_europe.*)

in the United States but also a substantial problem in China, Eastern Europe, Russia, and areas downwind of populated areas. Acid rain has become more widespread with industrial and population growth. Figure 3.3 illustrates areas in Western Europe that are susceptible to low pH rainfall.

If the lakes and reservoirs receiving this rainfall are already low in natural alkalinity, acidic lake water may result. This condition can lead to a sterile aquatic environment, unless the acidity is neutralized by application of lime, soda ash, or other alkaline material. In general, the lakes and reservoirs affected by acid rain are contained in basins with granite bedrock. These waters have little alkalinity, as shown earlier in Table 3.3, and can be quite corrosive even without the added input of acid rain.

Effects of Landfill Leachate

The disposal of both domestic (municipal) and industrial wastes as solids and packaged liquids in landfill areas is a common practice. In industrialized countries, the enormity of the risk this has created for groundwater contamination can be a major environmental issue, if the landfill is not properly constructed.

In the United States, the Environmental Protection Agency (EPA) is identifying hundreds of major sites that must be cleared, decontaminated, and restored to a nonhazardous status. Many of these sites owe their hazardous nature to the presence of toxic chemicals, usually leaking from damaged or partially drained shipping containers. Water-soluble materials are usually carried into the soil by storm water. In some cases, soil bacteria may digest organic chemicals. In the aerobic zone, the by-product is mostly carbon dioxide. However, if the leachate reaches the anaerobic zone, the by-products are ammonia, carbon dioxide, methane, and residual refractory organic materials.

In many cases, soil adsorbs some toxic substances like polychlorinated biphenyls (PCB) and pesticides until saturated, and then these materials continue downward until they reach and contaminate the water table. The soil must then be decontaminated.

Effects of Acidic Mine Drainage

When mines are abandoned, they often fill with water. The oxidation or bacterial decomposition of metal sulfides from the surrounding rock or tailings can produce very acidic water, which can carry high concentrations of metals, most commonly iron, copper, and zinc. Other metals, including nickel, lead, arsenic, aluminum, and manganese, can also contaminate mine drainage. Because of the low pH and metal ion content, this water can be very toxic to environmental organisms. Contaminated mine water can seep through the ground and increase metal ion concentrations in local areas. When contaminated mine water flows out of the mine, it can pollute rivers and lakes. The low pH and metal ion content can cause fish kills or destroy microbes and plants.

Impact of Water and Process Treatment

An attitude of conservation is taking hold across industries and water managers need to approach total plant water assessments with a framework that incorporates reduce-reuse-recycle objectives. A total site and system approach is essential to manage cost and improve environmental performance. Correct application of water and process treatment programs, including a combination of chemistry, monitoring and control services, and equipment, can make a major contribution to sustainable development of industrial and other operations. Proper water treatment can reduce demand for natural resources, deliver improvements to system efficiency, and improve a company's financial performance, while providing many environmental benefits:

- Cleaner water to use and air to breathe
- Increased energy efficiency, reducing fuel use and emissions of greenhouse gases
- Improved water recycling, leaving more freshwater for other uses

- Reduction in solid wastes and liquid emissions
- Improved environmental performance
- Sustainable development of site operations

Boiler Water

Boiler water treatment is essential in maintaining energy efficiency and integrity of steam and heat generating systems. Poor management of heat exchange surfaces and water use can have major effects on system performance, fuel demand, gas and water emissions, asset life, and all associated costs. This in turn affects environmental performance and ultimately sustainable development of the plant operation.

Boiler operation is a high-intensity use of energy and a key opportunity for environmental gains. By preventing corrosion, assets are protected and asset life extended, reducing replacement frequency and the consequent demand for more nonrenewable resources to replace it. Scale prevention and water management can give substantial environmental benefits through reducing fuel use and greenhouse gas emissions. This offers consequential economic benefits.

Improvement of boiler water treatment practices can offer significant benefits. Steam systems with an effective treatment program can operate 1 to 3% more efficiently than one with an ineffective treatment program. Although higher operating efficiency is one benefit, an effective program extends equipment life, improves system performance, and reduces risk of operating problems. All of this reduces resource use, emissions, and costs.

The impact of boiler tube scale and deposits can include:

- Loss of energy efficiency = more fuel = increased greenhouse gas emissions
- Risk of tube failure from overheating or corrosion
- Reduced steam purity
- Reduced steam system reliability

The approach to securing better environmental performance and increased cost savings includes identification and prioritization of opportunities for energy savings. Projects can be sorted according to areas where treatment programs and services can have the greatest positive impact. A combination of environmental and economic improvements can then make a significant contribution to sustainable development.

A summary of the linkage between boiler water treatment and sustainable development is shown in Fig. 3.4.

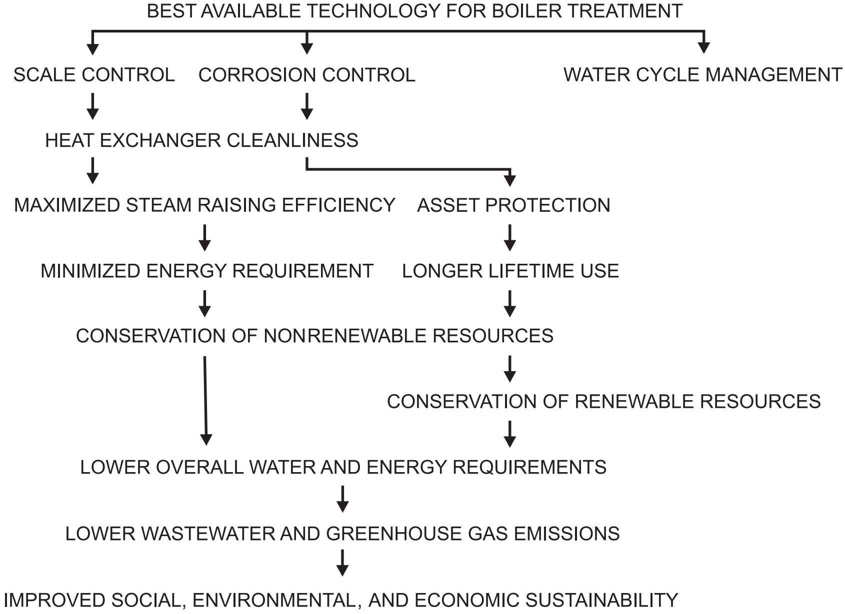

Figure 3.4 Linkage between boiler water treatment and sustainable development.

Cooling Water

Treatment of cooling water affects environmental protection and contributes to sustainable development. Programs target control of scale, corrosion, and microbiology, while improving water and energy management. This assures system cleanliness, minimizes water and energy use, controls emissions to air and surface waters, and maximizes asset life.

This in turn protects the local community and the environment through minimized resource demand and emission generation. Programs also support the plants own commitments to sustainable development, increasingly building stakeholder confidence (employee satisfaction, investor interest, and community respect).

In systems that rely upon heat transfer into cooling waters, impaired heat transfer can affect overall efficiency of the system and the processes or production linked to it. Proper application, control, and monitoring of a water treatment program can provide the correct level of ongoing protection and maintain system performance at required levels. Where necessary, the use of best practices in cleaning and system maintenance can assure cost-effective operations.

Failure to keep heat exchanger surfaces clean and free of scale deposits and corrosion can lead to significant reductions in heat transfer and cooling efficiency. In condenser systems, this has an immediate primary impact upon energy use and indirectly upon fuel use and greenhouse gas emissions. Secondary impacts can include reduced production capacity or even shutdown, equipment malfunction, and poor finished product quality. Clearly, any loss of efficiency can prejudice sustainability.

Biofouling or scale can insulate the heat transfer surface and prevent efficient cooling performance, and this is usually caused by inadequate treatment on either the water or process side. This can be prevented by proper treatment, control, and monitoring of the cooling system, and it can be remedied by "best practice" cleaning and treatment. Other factors can impair heat transfer into the cooling water and can be remedied with maintenance, cleaning, and treatment.

Correct treatment of cooling water maximizes asset life and minimizes economic and environmental impacts of replacement; minimizes fuel use and greenhouse gas emissions through scale and corrosion control; protects the population from potential illness through the effects of infection by *Legionella* bacteria; conserves both renewable and nonrenewable resources; and controls costs. This matrix shows the complex relationship between water treatment and some of the ultimate impacts upon sustainable development (Fig. 3.5).

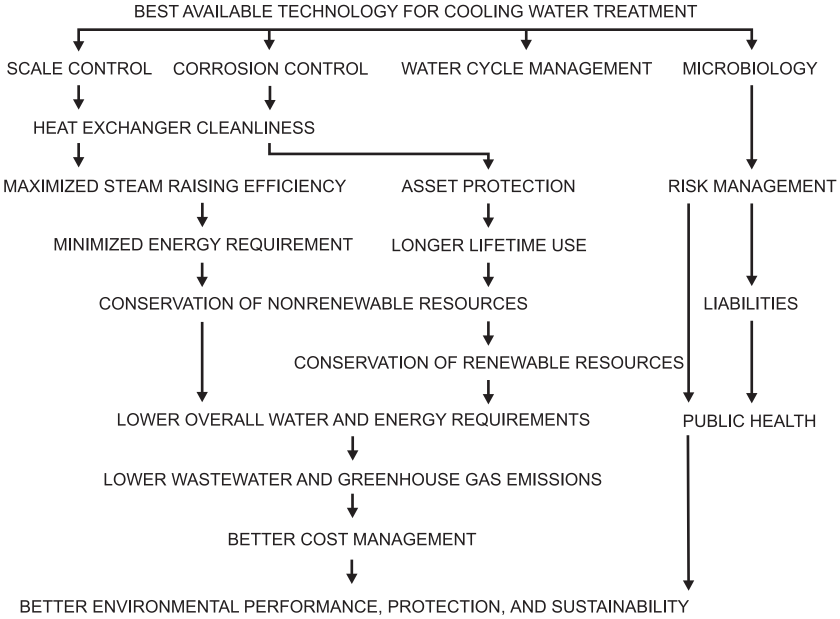

Figure 3.5 Linkage between condenser cooling water treatment and sustainable development.

Wastewater

With wastewater treatment, correct program delivery has a direct impact upon environmental performance and sustainability. It is important to understand plant activities that affect environmental performance; where the treatment program can affect these; what impact this has upon resource management, standards compliance, and cost management; and how this flows through to protection of the environment, better environmental performance, and sustainable development. The linkage between all these factors is shown in Fig. 3.6.

Focus on Total System Performance

Market-leading programs can represent a significant contribution to improving environmental performance of production units, through lower resource use, reduction in emissions, and innovative management of cost. This contributes to sustainable operation and development of processes by lowering demand for nonrenewable resources and reducing global warming potential through lowering greenhouse gas emissions. Improvements in profitability and environmental performance are a constant focus for plants.

Careful management of heated water resources affects both water resource use and energy costs and associated fuel use and gas emissions. This type of analysis can be very helpful in quantifying

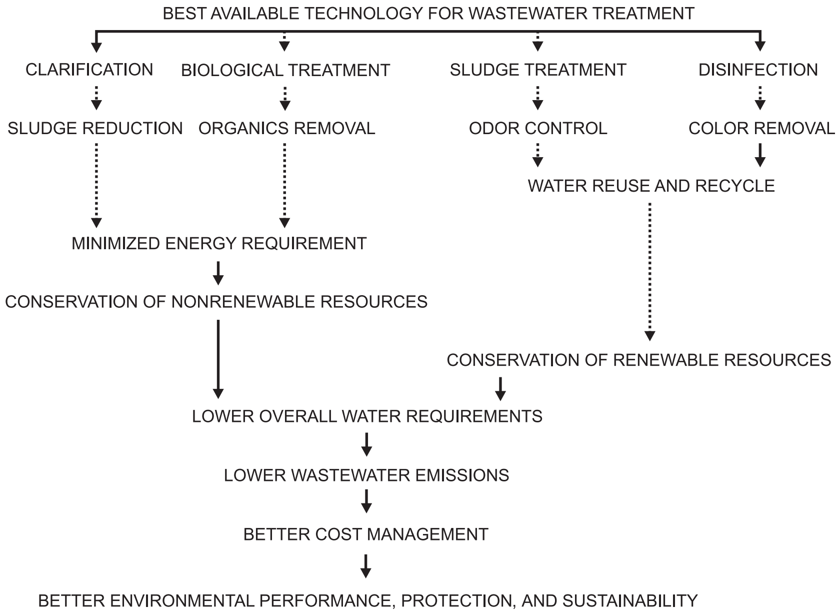

Figure 3.6 Linkage between wastewater treatment and sustainable development.

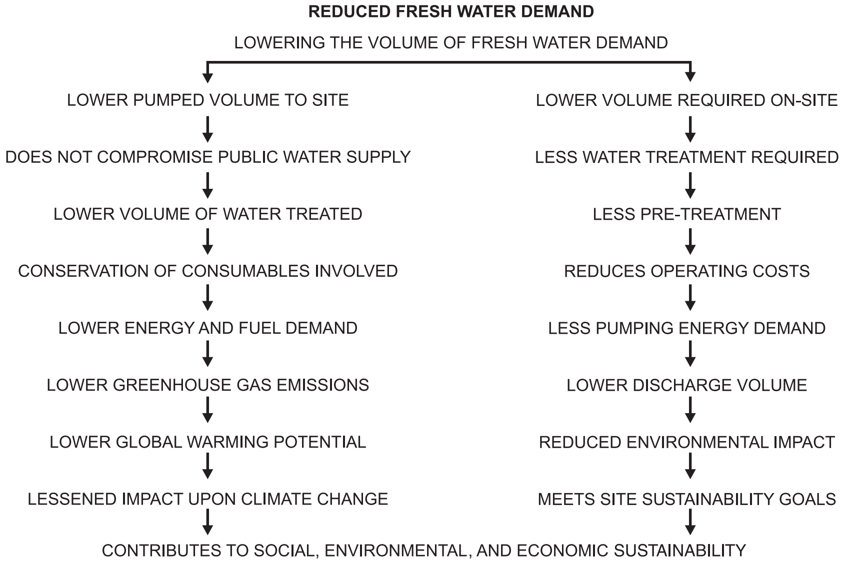

Figure 3.7 Impact of reduction in demand for fresh (makeup) water on sustainable development.

cost avoidance and savings opportunities, and justifying the investment in operational improvement projects.

Innovation in renewable materials for transportation is creating new alternatives to fossil fuels; however, many of the new manufacturing processes involved require large amounts of water. Precise management and treatment of water used insures that gains made through renewable fuel availability are not prejudiced by a greater demand for other resources. By managing the whole lifecycle, environmental and economic gains can be realized with the greatest benefits for society.

As a whole, proper application, monitoring, and control of water and process treatment programs can offer a wide range of benefits, and many of these are beyond the realm of traditional thinking. Figure 3.7 shows the impact of reduction in demand for fresh (makeup) water on sustainable development.

Proper water treatment, therefore, can be a significant source of economic value for industry—driving energy efficiency, waste reduction, improved material utilization, and other environmental and financial benefits in addition to water savings. A clear focus on proper water treatment allows full gains to be made by reducing, reusing, and recycling precious water resources.

SECTION 2

Basic Water Chemistry

CHAPTER 4 Water Chemistry	**CHAPTER 5** Impurities in Water

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CHAPTER 4

Water Chemistry

Chemistry involves the study and the interactions of atoms and molecules that make up all matter. Three aspects of matter considered to be of primary importance are the properties, composition, and transformation or reactions of matter. The physical properties of matter distinguish different substances. Water and alcohol are different substances due to different melting points, boiling points, and density. The second aspect is the composition of matter. This refers to the compounds, molecules, and atoms present in a substance and the relative ratios of those components. The last aspect is the transformation of matter from one substance to another. Simple examples are the combination of hydrogen and oxygen to make water or the transformation of iron ore into iron metal. The transformation of matter from one substance to another involves the exchange of energy, which may be given up, as in the case of burning fuel, or may be added, as in the case of generating steam from water.

At a higher level, the water chemist studies the nature and variable properties of water, and the effect of those properties on the application and use of water. Water is not a pure substance but a solution that can include many dissolved substances. Does the water source contain impurities that can lead to scaling? How does water chemistry affect corrosion of system metals? Can these impurities be easily removed by ion exchange, filtration, chemical reaction, etc., making the water more useful for industry or municipal use? This chapter will explore aspects of chemistry, from the basics to some key properties and interactions, which are necessary for a working knowledge of water chemistry.

Atoms, Molecules, Ions, and Compounds

The atom is defined as the smallest unit of matter retaining the characteristics of an element; a molecule is the smallest unit of matter retaining the properties of a compound. A variety of combinations and states exist:

- Atoms can form ions and combine into molecules.
- Molecules may be as simple as the association of two hydrogen atoms to form molecular hydrogen, or as complex as the combination of amino acids that make up deoxyribonucleic acid (DNA).
- Ions can be an atom or molecule, which has lost or gained one or more electrons, making it positively or negatively charged.
- A positively charged ion has fewer electrons than protons and is called a cation.
- A negatively charged ion has more electrons than protons and is called an anion.
- Molecules containing a number of different atoms or ions are called compounds.

Atoms and Molecules

The study of matter begins with the atom, the smallest particle characterizing a chemical element. The atom consists of an electron cloud surrounding a dense nucleus of protons and neutrons (Fig. 4.1). Protons have a positive charge, and neutrons are without charge. The positive charge of the nucleus is balanced by the negative charge of the electrons in the cloud around the nucleus. Chemical reactions between atoms or molecules involve only these electrons. The physicist is concerned with activity within the nucleus. The chemist is concerned with the properties and reactions of the atoms. For practical purposes, the mass of the atom must be considered the mass

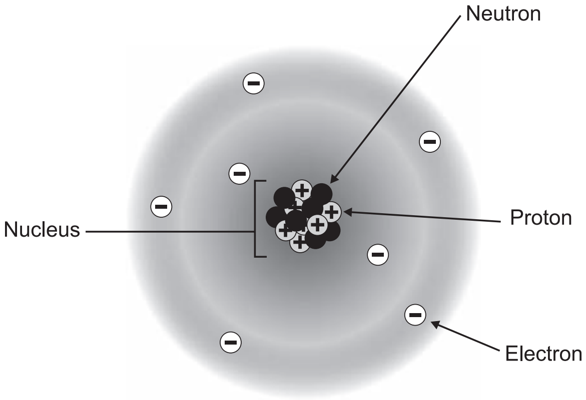


Figure 4.1 Illustration of the electron cloud model of an atom.

of the nucleus, since the electron is less than 0.02% of the mass of the proton.

Atoms are identified by name, atomic number, and atomic mass. The atomic number in an atom of neutral charge is the number of electrons in orbit around the nucleus, which is also the number of protons in the nucleus. The atomic mass of the atom is the sum of the protons and neutrons in the nucleus. The names and symbols are of historic interest and consist of both ancient and recent history. The symbol for lead (Pb) is from the Latin plumbum, from which is derived the word plumber, whereas fermium (Fm), atomic number 100, is named for Enrico Fermi. The general properties of elements can be grouped into a table that illustrates the repetition, or periodicity, of physical properties. This table is called the periodic chart of the elements (Fig. 4.2).

Bonding in Compounds

Molecules are combinations of elements or atoms bonded together to form the basic building blocks of compounds. Molecules contain at least two different atoms bonded together strongly enough to be a stable combination. Three types of bonding mechanisms may hold molecules together:

1. Ionic bonding (Fig. 4.3)
2. Covalent bonding (Fig. 4.4)
3. Coordinate covalent bonding (Fig. 4.5)

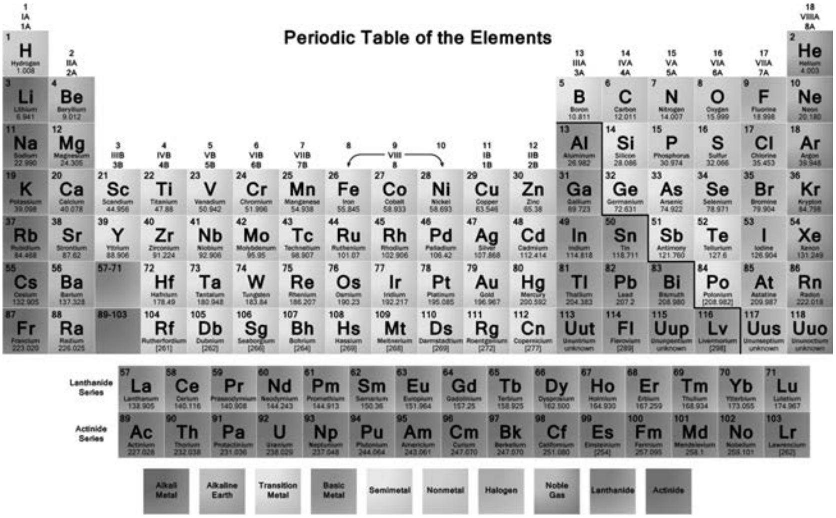


Figure 4.2 Periodic table of the elements.

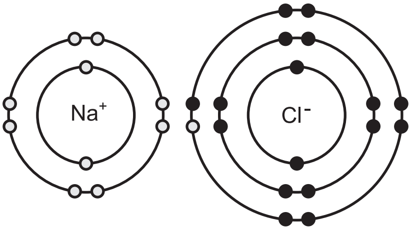


Figure 4.3 An ionic bond in sodium chloride is created when a sodium atom transfers an electron to a chlorine atom creating positive and negative ions held together by the force of the electrostatic attraction. (Note: The Bohr electron model is use for simplicity, although it is not an actuate model of electron orbital structure.)

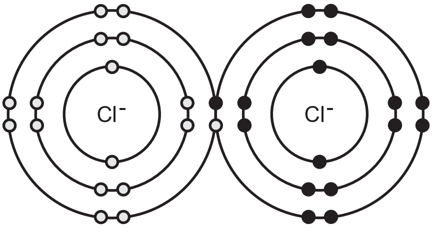


Figure 4.4 A simple example of covalent bonding illustrated by the diatomic molecule, chlorine, where the shared pair of electrons is attracted to the nucleus of both atoms. The electrons are all equal, even though they are represented by different shades of gray.

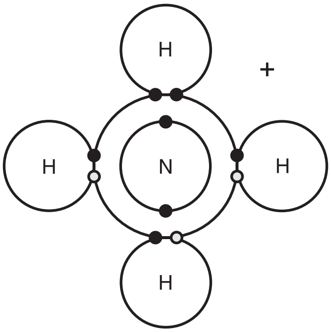


Figure 4.5 A coordinate covalent bond is a type of covalent bond where one atom donates both of the shared electrons to one bond, as illustrated in the ammonium ion. The two dark dots in the upper bond represent electrons donated by the nitrogen atom.

An ionic bond is formed between two oppositely charged ions. It typically forms between metal and non-metal ions through electrostatic attraction. Sodium chloride is an example of a metal and non-metal ionic bond. The metal (sodium) donates one electron, forming a positively charged cation. The electron enters the nonmetal (chloride), forming a negatively charged anion. Both cation and anion have stable electronic configurations. The attraction between the oppositely charged ions causes them to come together and form a bond. In general, ionic bonding occurs only if the overall energy change for the reaction is favorable. This is when the bonded atoms have a lower energy than the free ones.

The second type of bonding mechanism is the covalent bond. It is characterized by the sharing of pairs of electrons between atoms or molecules. The hydrogen molecule is an example of shared electrons via covalent bonding. Covalency is greatest between atoms that are similar, like the carbon-carbon bond in organic compounds. The most common type of covalent bond is the single bond, which is the sharing of only one pair of electrons. More than one electron pair is called a multiple bond. Double bonds are simply sharing two pairs of electrons. Triple bonds are sharing three pairs of electrons. Higher bonds exist for transition metals.

The third mechanism of bonding is actually an artificial one, in which both electrons come from the same atom. This type of bonding is called coordinate covalent bonding and is useful to describe coordination compounds. An example is the calcium cation with a +2 charge. In water, calcium coordinates with six water molecules and covalently shares six pairs of electrons.

Since the mass of atoms and molecules are relative and because the units themselves are very small, the chemist uses units called moles. A mole is an arbitrary unit given in grams. The number of grams in a mole of a given substance is determined by adding the atomic mass of the constituents. An example is calcium carbonate ($CaCO_3$), a compound very familiar to water chemists, having a molecular weight of 100 g/mol (grams per mole). This is also called the gram-molecular weight. The number of molecules in a mole of any substance is defined by Avogadro's number ($6.02 \cdot 10^{23}$/mol).

The Water Molecule

The proper study of water begins with the water molecule. The formula for water is H_2O, which by itself tells us only its composition and molecular weight. The water molecule is formed by the reaction between molecules of hydrogen and oxygen, as shown in Fig. 4.6. Water exists in liquid and solid states in addition to being found in the atmosphere as vapor.

Water's unique molecular arrangement (Fig. 4.6) shows two hydrogen atoms located 105° apart and adjacent to the oxygen atom.

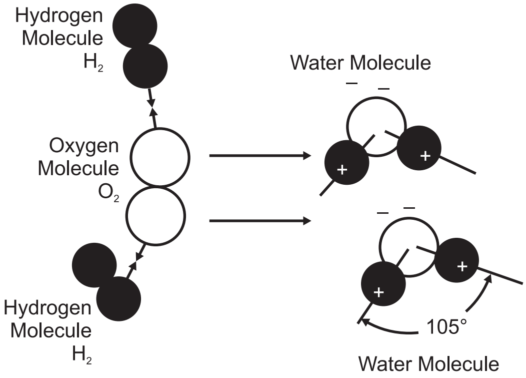


FIGURE 4.6 Reaction between hydrogen and oxygen molecules to form water molecules. The polar nature of the molecule is illustrated by the positive charges on the hydrogen ions and the negative charge on the oxygen ions.

The molecule is asymmetric with partial positive charges on the hydrogen atoms and partial negative charges on the oxygen atom. This causes the water molecule to be dipolar (opposite charges at opposite ends of the molecule). Many substances dissolve in water because of this polarity. Water in nature is rarely pure and can dissolve many inorganic and organic compounds. However, many compounds are insoluble in water, such as oils.

Solubility of Matter in Water

Water molecules surround charged particles and pull them into solution. Using sodium chloride (NaCl) as an example, water molecules work their way into the crystal lattice and between the individual ions. They surround the alternating sodium and chloride ions and slowly dissolve the salt (Fig. 4.7). The negative oxygen side of the

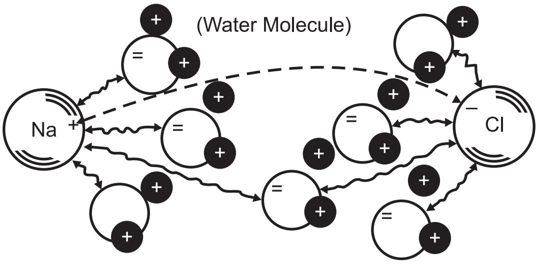


FIGURE 4.7 Dissolution and solvation of sodium chloride by dipolar water molecules.

water molecule surrounds the sodium ion, and the positive side of the molecule (hydrogen side) surrounds the chloride ion. The liberated ions are held in solution by this hydrating action and prevented from recombining. Oil, for example, does not dissolve in water because there is no net electrical charge across the molecule, making it a nonpolar molecule.

Hydrogen Bonding

The dipolar nature of the water molecule causes aggregation of water molecules. The hydrogen end of the molecule attracts the oxygen side of an adjacent molecule, linking them by an attractive force called hydrogen bonding (Fig. 4.8). In this manner, one water molecule is hydrogen bonded to four adjacent water molecules.

One of the consequences of hydrogen bonding is that molecules of water cannot leave the surface of a body of water as readily as they could without this intermolecular attraction. The energy required to break the hydrogen bond and liberate a molecule of water to form vapor is greater than for other similar chemical compounds. This leads to three important properties of water for industrial use:

1. The energy content of water vapor (steam) is high, making it a great heating source.
2. Water absorbs or releases more heat (higher heat capacity) for each incremental change in temperature than many substances, making it an effective heat transfer medium.
3. Water releases more heat upon freezing than many other compounds.

The freezing of water is unusual compared to other liquids. Most compounds become denser when frozen (solid) than in liquid form. Hydrogen bonding produces a crystal arrangement that causes ice to

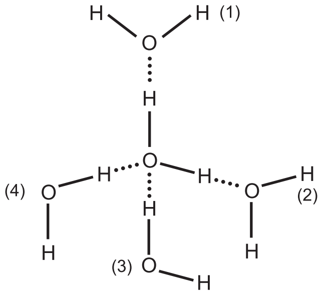


Figure 4.8 The dashed lines illustrate hydrogen bonding between water molecules. The hydrogen bond is much weaker than bonds between oxygen and hydrogen in the water molecule, but still strong enough to affect properties of water.

Substance	Specific Heat, Btu/[lb·°F] (kJ/[kg·°C])	Freezing Point, °F (°C)	Boiling Point, °F (°C)	Latent Heat of Evaporation, Btu/lb (kJ/kg)
Water	1.0 (4.18)	32 (0)	212 (100)	970 (2255)
Hydrogen Sulfide	0.24 (1.02)	–122 (–86)	–77 (–61)	237 (552)
Methanol	0.60 (2.51)	–144 (–98)	151 (66)	473 (1099)
Ethanol	0.65 (2.72)	–174 (–114)	172 (78)	364 (846)
Benzene	0.43 (1.80)	42 (6)	176 (80)	168 (391)

Table 4.1 Comparison of Physical Properties of Water to Similar Compounds

expand beyond its original liquid volume, so that its density is less than that of the liquid. As a result, ice floats on liquid water. If this was not the case, lakes would freeze from the bottom up, and life as we know it could not exist.

Because of the unusual structure of the water molecule, it is present in the natural environment in all three states of matter: solid as ice, liquid as water, and gas as vapor. It is the only chemical compound having this unusual character. Table 4.1 compares the boiling point and other heat-related properties of water with similar molecules, such as hydrogen sulfide (H_2S), and with other compounds that are liquid at room temperature.

Other Properties of Water

In addition to its unusual heat properties, water has physical properties quite different from other liquids. Its high surface tension is easily demonstrated by the experiment of floating a needle on the surface of water in a glass (Fig. 4.9). High surface tension, due to hydrogen bonding, causes water to rise in a capillary tube (Fig. 4.10). This capillarity is partly responsible for the system of circulation developed by living plants through their roots and tissue systems.

Pure, distilled water ionizes so very slightly, producing only 10^{-7} moles of hydrogen and 10^{-7} moles of hydroxyl ions per liter, that it is an insulator. Pure water does not conduct electrical current. As salts or other ionizing materials dissolve in water, electrical conductivity develops. The dissolved minerals in natural waters vary from place to place, and the conductivity is a measure of the dissolved solids (Fig. 4.11). For most public water supplies, the conversion factor is 1.55 µS/cm per mg/L of total dissolved solids. This conversion factor must be established for each situation and for other types of water, like wastewater and boiler water.

FIGURE 4.9 A steel needle, with a density about seven times that of water, can be made to float because of the high surface tension of water.

Another important phenomenon occurring in water solutions related to dissolved matter (solutes) rather than to the water (solvent) is osmotic pressure. If a membrane separates two aqueous solutions, water passes from the more dilute into the more concentrated solution. This important process controls the performance of all living cells. It explains the effectiveness of food preservation by salting. The salt creates a strong solution, disrupting cells of organisms that might cause food spoilage. Water inside their body leaves

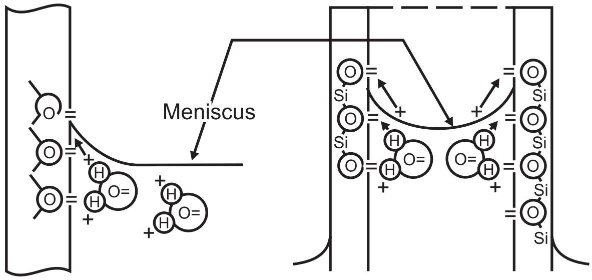


FIGURE 4.10 A meniscus forms (left) when hydrogen atoms reach upward to wet oxide surfaces of the glass tube at the water line. The drawing at the right shows how hydrogen bonding of water to a thin glass tube causes water in the tube to rise above the level of the surrounding water.

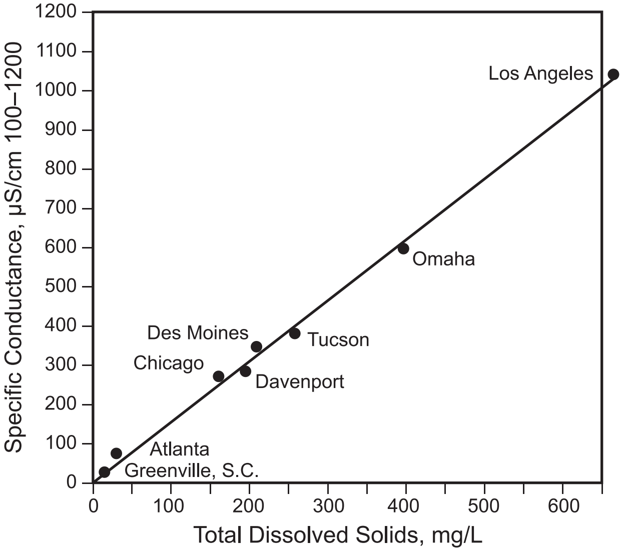


Figure 4.11 Dissolved solids content of water can be estimated from its specific conductance.

in an attempt to dilute the external salt solution. In specially designed membrane cells, the osmotic flow of water across the membrane can be reversed by applying a sufficiently high pressure to the more concentrated solution. This process of reverse osmosis is used for desalination of water.

Finally, viscosity is another property of water affecting its treatment and use. It is a measure of internal friction, the friction of one layer of molecules moving across another. As water temperature rises, this internal friction decreases. Because of the temperature effect, dissolved salts and gases can diffuse more rapidly through warmer water, chemical treatment is hastened, and the physical processes of sedimentation and degasification proceed faster. The effect of temperature on viscosity and surface tension (described earlier) is shown in Fig. 4.12.

Basics of Water Chemistry

The unique properties of water make it an ideal medium for industrial use, particularly for heat transfer applications. However, the solvent properties can create problems, like scale formation and corrosion. The ability to support life adds the opportunity for biological growth in some industrial water systems. An understanding of water chemistry is essential to combat these problems.

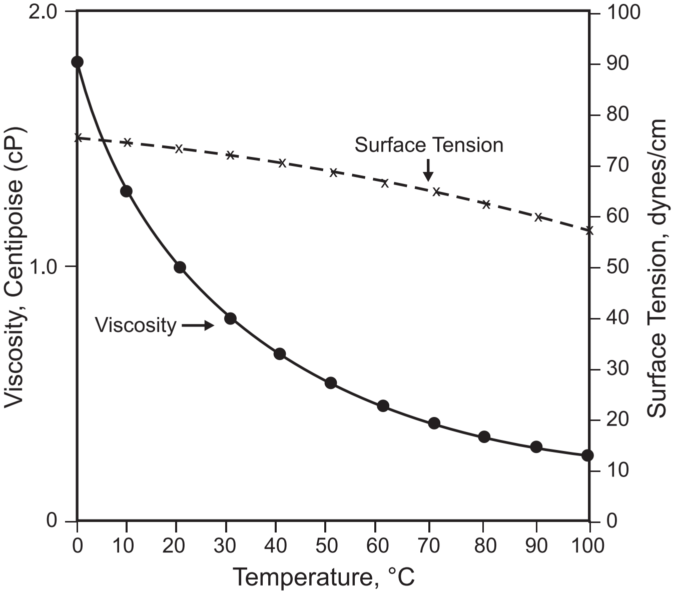


FIGURE 4.12 Surface tension and viscosity both decrease as water is heated.

Impurities in Water

Practically speaking, no chemical is pure, whether naturally occurring or artificial. The impurity level in freshwater is measured in milligrams per liter (mg/L), with 10 000 mg/L equaling 1%. A sample of good lake water having total dissolved solids of 150 mg/L has an impurity level of only 0.015%. Sometimes, parts per million (ppm) is used in place of mg/L to measure impurities in water. Since a liter of distilled water weighs 1000 g or 1 000 000 mg, it is apparent that 1 mg/L of an impurity represents 1 ppm. However, a liter of seawater weighs about 1032 g, and 1 mg of impurity in seawater is less than 1 ppm. Because the density of different waters and water solutions, like brines, can vary, the use of mg/L is more precise than ppm. This book will use mg/L, the preferred notation.

Anything in water that is not H_2O is a contaminant or impurity. The principal job of the water chemist is to define these impurities, set specifications for acceptable levels of each impurity based on the intended use of the water after treatment, and devise economical treatment methods to reach the quality limits that have been set. It is important to recognize that the terms impurity, contamination, and pollution are subjective qualities of water. In this book, a contaminant is considered a pollutant when its presence and concentration are harmful either to aquatic life, or to public health if the water is for potable purposes. Dissolved impurities in water are broadly classified as inorganic salts (dissolved from minerals in the geologic formations in contact with the water source) and organic matter (related to aquatic life and vegetative cover of the watershed). In most freshwaters, dissolved matter is largely inorganic.

Electrolytes

When water dissolves a mineral, ions of the mineral separate or dissociate in the solution to form cations and anions. Generally, an increase in water temperature causes an increase in the solubility of most salts, like sodium chloride (NaCl) or potassium sulfate (K_2SO_4). Important and notable exceptions are calcium carbonate ($CaCO_3$), calcium sulfate, anhydrite ($CaSO_4$), magnesium carbonate ($MgCO_3$), and magnesium hydroxide [$Mg(OH)_2$], all of which become less soluble as temperature increases (Fig. 4.13).

A simple demonstration of ionization is an experiment in which an electric light is connected to a circuit with two separated electrodes inserted in a beaker of water (Fig. 4.14). In pure water, the lamp does not light when the switch is on, because pure water is an insulator not a conductor. Salt is added to the water in small increments, and gradually the light brightens. The light intensity is proportional to the amount of salt added. Current begins to flow only after sodium

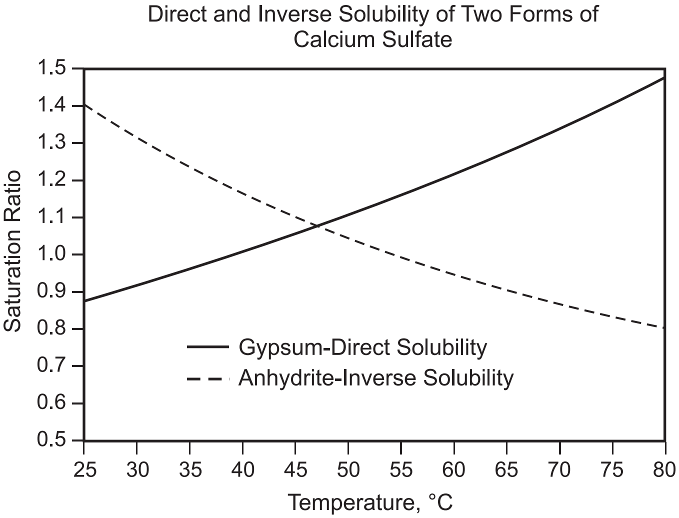


FIGURE 4.13 Solubility of some minerals increases with temperature (direct solubility) while other minerals have decreasing solubility with increasing temperature (inverse solubility).

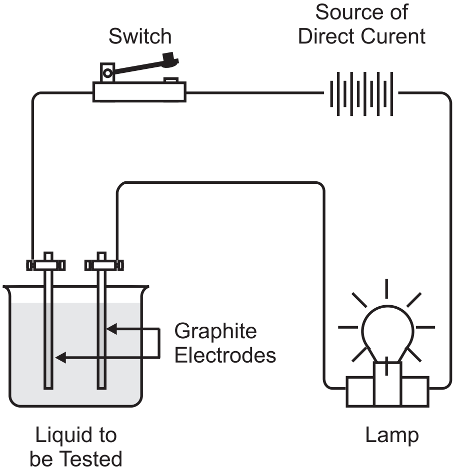


FIGURE 4.14 Pure water is nonconductive, but addition of an ionizing salt allows current to pass.

and chloride ions from the salt are present to transport electrons through the solution. If crystals of sugar are added to the water instead of salt, nothing happens; salt is an electrolyte, and sugar is not. Sugar is a polar organic compound that does not dissociate into ions when it dissolves.

High concentrations of impurities are known to lower the freezing point of water. For example, 1 mol/L of a nonelectrolyte such as sugar or alcohol dissolved in water lowers the freezing point by 3.35°F (1.86°C). However, 1 mol/L of sodium chloride lowers the freezing point by almost twice the value found for sugar and alcohol, and 1 mol/L of sodium sulfate produces almost three times this temperature depression. This is due to the production of multiple ions in solution from the salts, compared to only one dissolved molecule from sugar or alcohol. Each molecule of sodium chloride produces two ions, and one molecule of sodium sulfate (Na_2SO_4) produces three ions.

Elements in specific groups of the periodic chart become either cations or anions, depending on the group of elements (Fig. 4.2). Some of the elements that form cations in aqueous solution belong to the following groups:

- Alkali metals (lithium, sodium, potassium, etc.)
- Alkaline earth metals (magnesium, calcium, strontium, etc.)
- Some transition metals (iron, manganese, zinc, etc.)

Some of the elements that form anions in aqueous solution belong to the following groups:

- Halogens (fluorine, chlorine, bromine, etc.)
- Other nonmetals (oxygen, sulfur, selenium, etc.)

Electromotive Series

In their elemental form, alkali metals and alkaline earth metals can displace hydrogen from aqueous solutions. Sodium and potassium are so active that they react with water itself to liberate hydrogen:

$$2\text{Na} + 2\text{H}_2\text{O} \rightarrow \text{H}_2\uparrow + 2\text{NaOH} \tag{4.1}$$

Magnesium does not react with cold water, but it does react with acid, which releases hydrogen in a solution:

$$\text{Mg} + 2\text{HCl} \rightarrow \text{H}_2\uparrow + \text{MgCl}_2 \tag{4.2}$$

Cations can be classified according to their reactivity in an order known as the electromotive series, shown in Table 4.2. Not only will the more reactive metals displace hydrogen from solution, but they even displace metals below them in the series. For example, if a strip of iron metal is placed in a solution of copper sulfate, copper ions deposit on the iron strip as copper metal, as the iron dissolves into solution by the following reaction:

$$\text{Fe}^\circ + \text{CuSO}_4 \rightarrow \text{Cu}^\circ + \text{FeSO}_4 \tag{4.3}$$

In comparing reactions (4.1) and (4.2), to produce one molecule of hydrogen requires two atoms of sodium but only one atom of magnesium, because sodium has a charge of +1, while the magnesium ion has a charge of +2. This provides one basis for the concept of equivalent weight. The equivalent weight of a cation is that weight which replaces 1.0 g of hydrogen from aqueous solution. Another way to determine equivalent weight is the molecular weight of a substance divided by its valence. Thus, the equivalent weight of sodium is equal to its molecular weight, and the equivalent weight of magnesium is half its molecular weight. Table 4.3 shows the molecular weights and equivalent weights for common compounds encountered in water treatment.

Colloidal Systems

Some types of matter can be dispersed in water even though not truly soluble. Dispersion is accomplished by breaking down the material into extremely small particles, slightly larger than ions and molecules. Particles of this size, suspended in liquid, are called colloids.

Element	Half-Cell Reactions	Standard Electrode Potential (V)
Potassium (K)	$K^+ + e^- \rightarrow K$	–2.93
Calcium (Ca)	$Ca^{+2} + 2e^- \rightarrow Ca$	–2.87
Sodium (Na)	$Na^+ + e^- \rightarrow Na$	–2.71
Magnesium (Mg)	$Mg^{+2} + 2e^- \rightarrow Mg$	–2.36
Aluminum (Al)	$Al^{+3} + 3e^- \rightarrow Al$	–1.66
Zinc (Zn)	$Zn^{+2} + 2e^- \rightarrow Zn$	–0.76
Iron (Fe)	$Fe^{+2} + 2e^- \rightarrow Fe$	–0.44
Nickel (Ni)	$Ni^{+2} + 2e^- \rightarrow Ni$	–0.25
Tin (Sn)	$Sn^{+2} + 2e^- \rightarrow Sn$	–0.14
Lead (Pb)	$Pb^{+2} + 2e^- \rightarrow Pb$	–0.13
Hydrogen (H)	$2H^+ + 2e^- \rightarrow H_2$	0.0
Copper (Cu)	$Cu^{+2} + 2e^- \rightarrow Cu$	0.34
Mercury (Hg)	$Hg^{+2} + 2e^- \rightarrow Hg$	0.79
Silver (Ag)	$Ag^+ + e^- \rightarrow Ag$	0.80
Gold (Au)	$Au^{+3} + 3e^- \rightarrow Au$	1.50

Table 4.2 Electromotive Series of Elements That Form Cations in Solution. The Voltage Is that Developed by an Electrode of the Element Immersed in a Molal Solution (1 Mole of Ion/kg of Water)

Common Name	Formula	Molecular Weight (g/mol)	Equivalent Weight (g/eq)
Table salt	NaCl	58.5	58.5
Caustic soda	NaOH	40	40
Salt cake	Na_2SO_4	142	71
Soda ash	Na_2CO_3	106	53
Limestone	$CaCO_3$	100	50
Quicklime	CaO	56	28
Slaked lime	$Ca(OH)_2$	74	37
Gypsum	$CaSO_4 \cdot 2H_2O$	172	86
Muriatic acid	HCl	36.5	36.5
Sulfuric acid	H_2SO_4	98	49
Aqua ammonia	NH_4OH	35	35

Table 4.3 Molecular Weights and Equivalent Weights of Common Water Treatment Compounds

The surface of almost all matter (glass, steel, plastic, etc.) has a residue of electric charges. This can lead to the development of high surface voltage, as demonstrated on a small scale by the discharge of a spark of static electricity on a cold dry day and on a large scale by lightning. As particles become smaller, the ratio of surface charge to mass increases exponentially. Assume that a cube of sand measuring 1.0 mm on each side is reduced to colloidal cubes of 100 nm (1 nm = 10^{-6} mm) on each side; this would produce 10^{12} colloidal particles with a total surface 10 000 times larger than the original grain with a correspondingly larger surface charge. It is this high surface charge that causes colloidal particles to repel one another, thus maintaining stability of the dispersion.

Solubility of Gases in Water

Like minerals, gases are soluble in water. Henry's law states that the amount of gas dissolved in water at a given temperature is directly proportional to the partial pressure of the gas above the water surface. Yet, each gas has its own solubility limit in water, just like any mineral. The atmosphere is approximately 20% oxygen and 80% nitrogen. At one atmosphere pressure [14.7 psia (101.35 kPaa)], the partial pressure of oxygen is 2.94 psia (20.27 kPaa), and the partial pressure of nitrogen is 11.76 psia (81.08 kPaa). At these partial pressures and standard temperature, the approximate concentration of oxygen in water is about 10 mg/L, while nitrogen is about 15 mg/L. Even though the partial pressure of nitrogen is four times higher than oxygen, less than twice as much goes into solution. If the total gas pressure at the water surface doubles, so would the concentration of oxygen and nitrogen in the water solution. Unlike most mineral salts, which become more soluble at higher temperatures, gases decrease in solubility as temperature rises.

Some gases react with water when in solution. For example, carbon dioxide (CO_2) reacts to form carbonic acid (H_2CO_3), which ionizes to produce hydrogen (H^+) and bicarbonate (HCO_3^-) ions [Eq. (4.4)]. Other ionizing gases include sulfur dioxide, hydrogen sulfide, and hydrocyanic acid, which form weak acids when dissolved in water.

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^- \tag{4.4}$$

On the other end of the scale is ammonia, which dissolves and ionizes to form a weak base:

$$NH_3 + H_2O \leftrightarrow NH_4OH \leftrightarrow NH_4^+ + OH^- \tag{4.5}$$

These are both equilibrium reactions, meaning that addition of more gas to the water produces more acidic conditions in Eq. (4.4) and more basic conditions in Eq. (4.5). On the other hand, addition of acid would drive Eq. (4.4) to the left. Similarly, addition of base in Eq. (4.5) would drive that reaction to the left.

Organic Compounds and Solubility in Water

Organic matter is a broad category that includes both natural and synthetic molecules containing carbon, usually hydrogen, and often other atoms like oxygen. All living matter is made up of organic molecules, and a wide variety of synthetic chemicals are organic. Organics can be extremely soluble in water (as is the case with alcohol and sugar) or may be quite insoluble (as are most plastics).

Most organics are unwanted contaminants in water. They can foul water systems, be food for bacteria that also cause fouling, or have harmful effects on aquatic life. Even at concentrations less than 1 mg/L, certain organic compounds may cause serious physiological effects. Modern technology makes it possible to analyze toxic organic materials such as pesticides at the μg/L level (1 μg of contaminant per liter of water). To put this in perspective, analyzing 1 μg/L is comparable to seeing a bottle cap on the earth's equator from an orbiting satellite.

There are an astounding variety of organic compounds in water, resulting from both nature and human activity. Many organic compounds in water are naturally occurring, like tannin and lignin from decaying wood. Tannin and lignin are generally present as colloidal suspensions in water. A water analysis does not show all of the individual organic molecules in a water sample, because of the great variety of compounds that may be present. Generally, an analyst looks for specific compounds, like polychlorinated biphenyls (PCB) or adsorbable organic halogen (AOX) using a special analytical method for each type of compound.

A variety of nonspecific tests are used to give a measure of the organic content of water. Examples of these methods include biochemical oxygen demand (BOD), total organic carbon (TOC), and color. Interpretation can be difficult, because these analyses cannot easily convert to a concentration of typical organics. In addition, these analyses may not follow the same pattern of increase or decrease over time in a given water. Figure 4.15 shows the diversity of change in color, TOC, and BOD in the Hackensack River in New Jersey, United States.

Solubility Product Constants

There are a few rules-of-thumb to use in determining the solubility of any chemical compound in water:

- The salts of sodium, potassium, and ammonium are highly soluble.
- Mineral acids (H_2SO_4, HCl, etc.) are soluble.
- Most halides (Cl, Br, I, etc.) are soluble, except for fluoride.

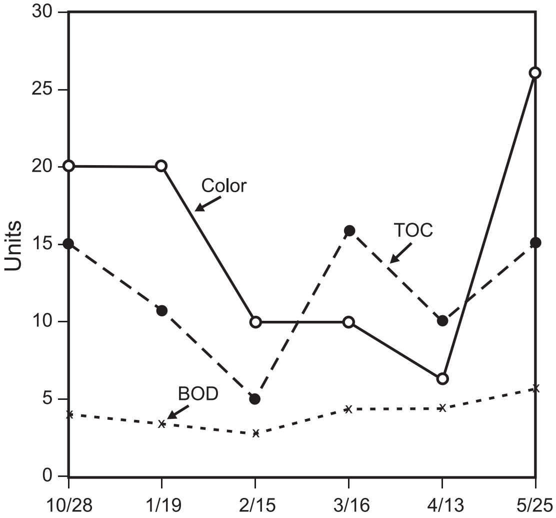


Figure 4.15 Variation of color, TOC, and BOD in the Hackensack River in New Jersey, United States.

- Certain heavy metal cations (Pb and Ag) form insoluble halides.
- Most carbonates, hydroxides, and phosphates are only slightly soluble, with the exception of those associated with Na^+, K^+, and NH_4^+.

According to the solubility product concept, the concentration of cations multiplied by the concentration of anions gives a product, which is a constant at a given temperature. For calcium carbonate, a simple example, this expression would be:

$$K_s = [Ca^{+2}][CO_3^{-2}] \tag{4.6}$$

The ions in square brackets indicate the concentration of either calcium or carbonate in mol/L. The solubility product is expressed in mol^2/L^2. In a reaction where more than a single cation and anion are formed, the expression is more involved, as with magnesium hydroxide:

$$Mg(OH)_2 \leftrightarrow Mg^{+2} + 2OH^- \tag{4.7}$$

$$K_s = [Mg^{+2}][OH^-]^2 \tag{4.8}$$

The units of K_s for magnesium hydroxide are mol^3/L^3.

In the case of $CaCO_3$, this mathematical expression is the equation for a hyperbola (Fig. 4.16). The solubility of calcium carbonate is determined by the calcium and carbonate concentrations at any given

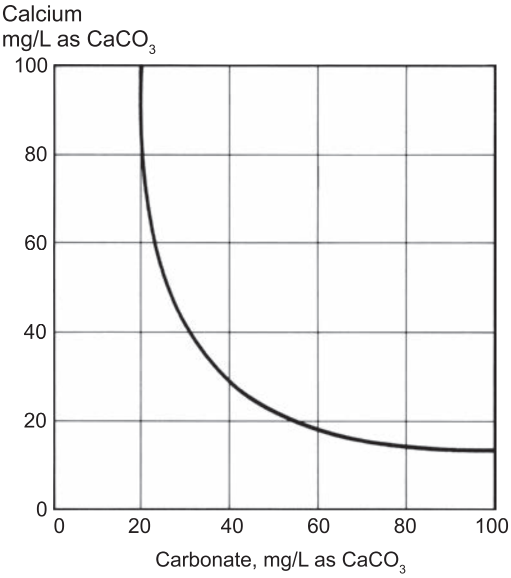


FIGURE 4.16 Curve showing the balance of calcium ions versus carbonate ions in saturated $CaCO_3$ solutions forms hyperbola.

point on the curve. The introduction of extra carbonate ions reduces the calcium concentration, at a given temperature, since the solubility product is constant. The solubility product makes it possible to calculate the residual solubility of a chemical after chemical treatment to remove a mineral from water by precipitation.

Foreign Ion Effect

Ions in solution can associate themselves with one another. For example, calcium may be present in water as Ca^{+2}, or it may exist as $CaHCO_3^+$ or $CaOH^+$. Magnesium may be present in a variety of ionic forms, for example, Mg^{+2} and $MgHCO_3^+$. The formation of ion pairs and other types of complexes in solution can significantly affect the solubility of minerals like calcium carbonate.

Because of the great variety of ions in most water systems, a pure precipitate, such as $CaCO_3$, rarely forms. The inclusion of foreign ions in the precipitate and the formation of a variety of ion pairs in the solution, in effect, increase the solubility of $CaCO_3$. Even if pure $CaCO_3$ precipitates, it may form two kinds of crystals, calcite (the more stable) and aragonite, which have different solubility. Therefore, the solubility product is of limited value in predicting actual treatment results. More detail on this will be given later in this chapter, in the discussion of calcium carbonate solubility.

Other Effects on Solubility

Another factor affecting solubility is the presence of organic matter dissolved in water. It is well known that the residual calcium from lime softening of sewage at ambient temperature is 2 to 3 times the calcium solubility in freshwater. This increased calcium solubility presumably is due to organic complexes. If the same sewage is heated over about 150°F (66°C), the reactions with lime are about the same as obtained with freshwater. Inexplicably, the same effect is not observed with magnesium precipitation.

One example of complex effects on precipitation is found in the coagulation of water with alum [$Al_2(SO_4)_3 \cdot 18H_2O$], where the following reaction would be expected:

$$Al_2(SO_4)_3 + 6H_2O \rightarrow 2Al(OH)_3\downarrow + 3H_2SO_4 \tag{4.9}$$

However, analysis of the precipitated floc shows the presence of sulfate in the solids, indicating that some SO_4^{-2} anions replaced OH^- anions in the lattice of the precipitate. This affects the solubility of aluminum hydroxide.

A final factor affecting solubility of these slightly soluble compounds is the ionic strength of the aqueous solution. The higher the concentration of ions in solution, the more soluble is the precipitate. This means that $CaSO_4$, for example, is more soluble in seawater, containing about 30 000 mg/L NaCl, and in oilfield brines, containing up to 150 000 mg/L NaCl, than in freshwater containing 100 mg/L dissolved solids. The solubility increase with ionic strength is shown in Fig. 4.17. The solubility product then, is seen to be a useful concept when used qualitatively, or developed empirically for a specific system, but of limited value when taken directly from a handbook.

Equilibrium

Another concept closely related to the solubility product is the equilibrium constant, also called the dissociation constant. Some reactions go to completion, using all of the reactants, assuming they are in the proper proportion. Not all chemical reactions go to completion, because the products of the reaction exert a restraining effect on the reactants.

An example of a reaction that goes to completion, sometimes explosively, is shown in Eq. (4.10). The arrow shows this reaction going in only one direction.

$$2H_2 + O_2 \rightarrow 2H_2O \tag{4.10}$$

An example of an equilibrium reaction is the precipitation of calcium carbonate, in Eq. (4.11). In this reaction, the precipitation of calcium

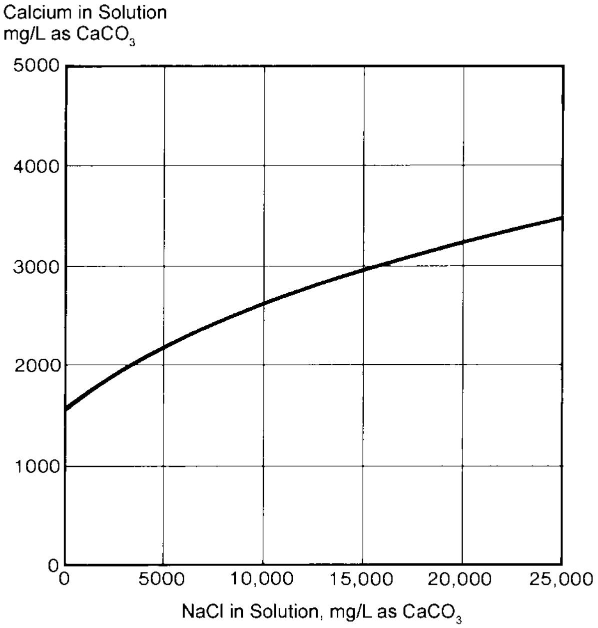


FIGURE 4.17 Calcium sulfate (gypsum) solubility increases with increasing sodium chloride concentration.

carbonate is balanced by the dissolution of calcium carbonate, as illustrated by the arrow pointing in both directions. At equilibrium, the rate of precipitation is exactly equal to the rate of dissolution.

$$Ca^{+2} + CO_3^{-2} \leftrightarrow CaCO_3 \tag{4.11}$$

This equilibrium reaction can be expressed mathematically by the equation for the equilibrium constant (K):

$$K = [Ca^{+2}][CO_3^{-2}]/[CaCO_3] \tag{4.12}$$

Recall that the bracketed values are expressed in concentration units, usually mol/L.

For the dissociation of electrolytes in water, the degree of ionization can be calculated, as shown for the reactions in Table 4.4.

Strong electrolytes, such as sodium chloride, completely ionize in freshwater, so that the equilibrium constant is of no value in calculations involving this particular salt. However, calculations involving weak electrolytes rely on the equilibrium constant to show the distribution of the reacting materials and products both in their ionic and nonionized forms. This provides data useful in selecting chemical processes for removal of various contaminants

Reaction	Degree of Ionization
$NaCl \leftrightarrow Na^+ + Cl^-$	0.85
$Na_2CO_3 \leftrightarrow 2Na^+ + CO_3^{-2}$	0.70
$HCl \leftrightarrow H^+ + Cl^-$	0.92
$H_2CO_3 \leftrightarrow H^+ + HCO_3^-$	0.0017
$NaOH \leftrightarrow Na^+ + OH^-$	0.91
$NH_4OH \leftrightarrow NH_4^+ + OH^-$	0.013

Table 4.4 Degree of Ionization of Electrolytes [0.1 Normal Solution at 64°F (18°C)], Showing That Some Compounds Are Highly Ionized and Others Are Only Slightly Ionized in Water

from water. For example, the equilibrium constants for gases that ionize in water, such as hydrogen sulfide and ammonia, make it possible to calculate the optimum pH values for removal of these materials from water in their gaseous form. Typical dissociation constants are shown in Table 4.5.

Solid Reactants

There are two distinctive mechanisms by which materials dissolved in water react with solids: adsorption and ion exchange.

Adsorption

Adsorption is the adhesion of a layer of molecules or colloidal particles to the surface of a solid, which is usually porous. The gas mask is a common illustration of the use of this process. The mask contains a canister of adsorbent material, usually activated carbon, capable of removing and storing hazardous or toxic gases, so that the person

Compound	Formula	Dissociation Constant
Calcium hydroxide	$Ca(OH)_2$	$3.74 \cdot 10^{-3}$
Phosphoric acid	H_3PO_4	$7.5 \cdot 10^{-3}$
Lead hydroxide	$Pb(OH)_2$	$9.6 \cdot 10^{-4}$
Ammonium hydroxide	NH_4OH	$1.8 \cdot 10^{-5}$
Acetic acid	CH_3COOH	$1.8 \cdot 10^{-5}$
Carbonic acid	H_2CO_3	$4.3 \cdot 10^{-7}$
Hypochlorous acid	$HOCl$	$3.5 \cdot 10^{-8}$
Boric Acid	H_3BO_3	$5.8 \cdot 10^{-10}$

Table 4.5 Dissociation Constants of Weak Acids and Bases

wearing the mask can safely breathe in a contaminated atmosphere. In water systems, activated carbon removes organic molecules that cause taste and odor problems. Another example is the adsorption of silica (SiO_2), a negatively charged colloid, on freshly precipitated magnesium hydroxide [$Mg(OH)_2$].

The amount of adsorbent required for effective removal cannot be universally determined for all waters from a single equation. However, for any given system, experimental data are easily plotted on a semi-logarithmic graph, producing a straight line. This graph is known as the Freundlich isotherm (Figs. 4.18 and 4.19). An equation unique to a given system can be determined from the graph and then used for dosage adjustment.

Ion Exchange

Ion exchange is the process of removing unwanted ions from solution by an equivalent exchange for preferred ions supplied by a solid having a special structure. The solid is an ion exchange material that

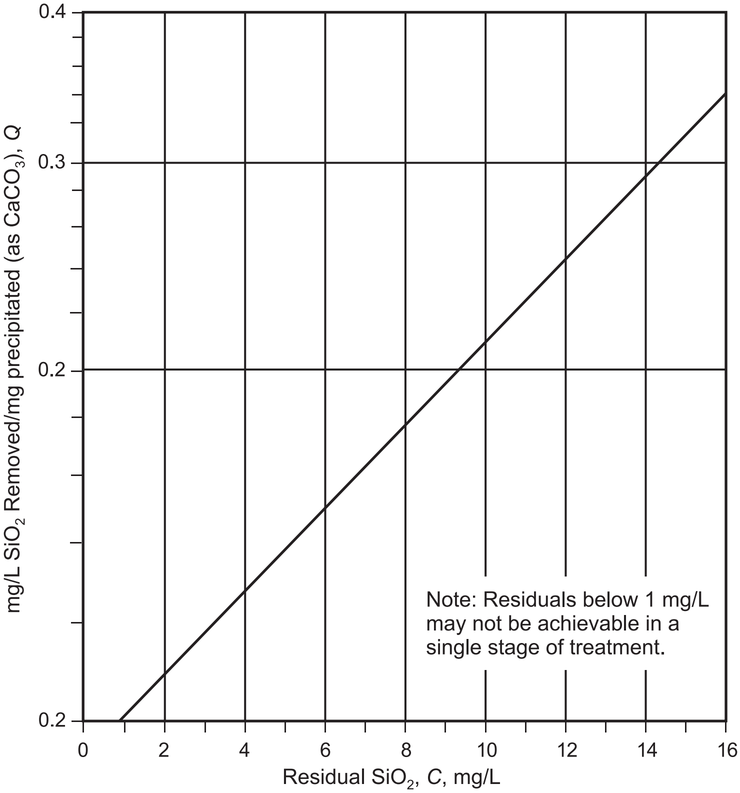


FIGURE 4.18 Freundlich isotherm showing effectiveness of SiO_2 adsorption by $Mg(OH)_2$. The formula for the isotherm is $Q = kC^{1/N}$.

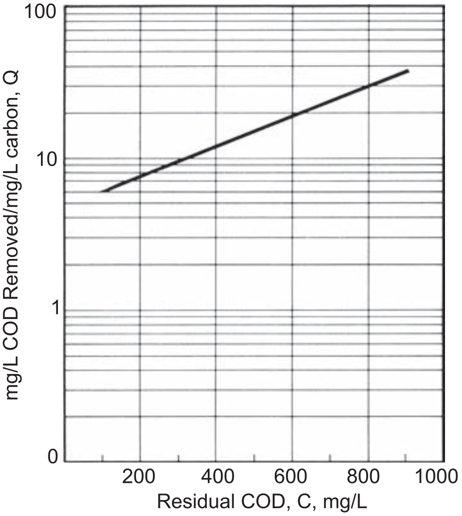


FIGURE 4.19 Freundlich isotherm showing effectiveness of organic adsorption (COD) by activated carbon. The formula for the isotherm is $Q = kC^{1/N}$.

has a stronger binding affinity for the unwanted ion. This ion exchange material must be recharged periodically with the preferred ions. In this regeneration, the accumulated, unwanted ions are flushed to waste. Removal of calcium ions by sodium ion exchange is shown by the following reaction, where the letter X represents the cation exchange solid:

$$Ca^{+2} + Na_2X \rightarrow CaX + 2Na^+ \tag{4.13}$$

Many types of clay have ion exchange properties. This is an important aspect of soil chemistry and plant nutrition. One of these clays, clinoptilolite, is used to remove ammonia from wastewater. However, most ion exchangers are synthetic organic materials formulated for specific applications.

Complexing Agents

A complex is a species formed by the association of two or more simpler species, each capable of independent existence. When one of these species is a metal ion, the resulting entity is known as a metal complex. Complexing agents are called ligands (or sequestrants or chelants) that act as an electron donor in a complex reaction. The ligand must have at least one pair of electrons to donate to the metal ion, forming a shared electron pair bond (coordinate covalent bond). A characteristic feature of such a complex is that the metal ion occupies a central position in the matrix.

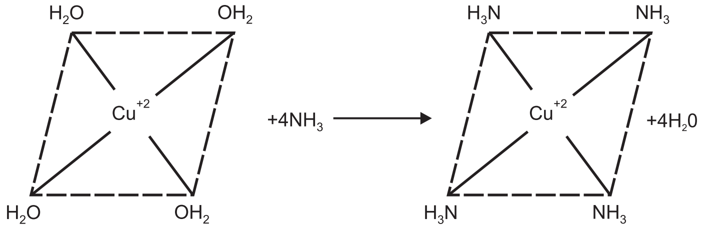


FIGURE 4.20 Example of a Cu^{+2} complex with ammonia.

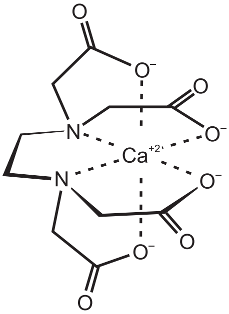
A ligand with one electron pair donor site is an undentate ligand. An example is ammonia (NH_3) as shown in Fig. 4.20. The water molecule (H_2O) is shown as a ligand. A bidentate ligand has two electron pair donor sites, such as ethylenediamine ($NH_2CH_2CH_2NH_2$). The donor sites are the nitrogen atoms, when complexed with copper (Cu^{2+}). The ethylenediamine forms a five-member ring with copper. This is a chelate ring. When this ring system forms, it adds stability to the complex. A multidentate ligand has two or more electron pair donor sites. Examples of common chelates used in water treatment are nitrilotriacetic acid (NTA) and ethylenediaminetetraacetic acid (EDTA). Both form multiple chelation rings with metal ions.

A chelating agent is usually an organic molecule, which is soluble in water and undergoes reactions with metal ions that maintain the complexed ions in solution. A common chelate is the sodium salt of EDTA. Added to water, this chelant first reacts with a coordination site on the calcium cation, which forms a coordinate covalent bond, pulling the rest of the molecule into the coordination sphere. These interactions prevent the formation of $CaCO_3$ scale in water as follows:

$$Ca^{+2} + Na_4EDTA \rightarrow CaEDTA^{-2} + 4Na^{+} \qquad (4.14)$$

Figure 4.21 shows the coordination complex formed with calcium. The bonding is through the nitrogen atoms of the ethylenediamine

FIGURE 4.21 Calcium-EDTA complex, with the coordinate covalent bonds shown by the dashed lines.



backbone of the chelant and through the oxygen atoms of the four acetic acid functional groups.

Low molecular weight polyacrylate-based polymers can complex hardness ions in water by the same mechanism as chelates. The molecular weight of these polymers is typically in the range of 1000 to 10 000 g/mol, although other size polymers can be used. Example reactions are:

$$\mathrm{Ca^{+2} + (polymer)^{-40} \rightarrow Ca(polymer)^{-38}} \tag{4.15}$$

$$\mathrm{Ca^{+2} + Ca_9(polymer)^{-22} \rightarrow Ca_{10}(polymer)^{-20}} \tag{4.16}$$

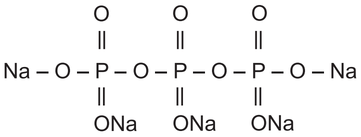
Although at room temperature, polyacrylates form weaker complexes than EDTA and NTA, based on experimental and field boiler results, it has been found that they form stronger complexes at elevated temperatures. The synthetic polyacrylate polymers are significantly less corrosive to boiler internals than chelates.

Low molecular weight polymers are excellent dispersants, which may operate by complexation. When compounds precipitate, they are usually deficient in one of the counter ions. This causes an imbalance of charge for a hydrophilic particle or colloid. Iron hydroxides are an excellent example. In industrial applications, iron corrodes to form ferrous hydroxide and ferric hydroxide. When this occurs, the system is usually deficient in hydroxide ions, resulting in an ineffectively shielded central metal ion, creating a positive surface attraction. Negatively charged polymers are attracted and adsorbed, shielding the central metal ion and increasing the surface partial negative charge. Like charge particles repulse each other, leading to dispersion.

On the other hand, very high molecular weight polymers (molecular weight in the millions) are used to neutralize surface charge on suspended material in water, leading to coagulation and settling of particles. This process is used in pretreatment for both industrial and municipal applications, as well as waste treatment operations.

A number of natural organic materials in water such as humic acid, tannins, and lignin have complexing ability. Because of their complexing abilities, some organic materials interfere with certain water softening processes.

Somewhat related to complex formation is the process of threshold treatment. A variety of phosphate compounds called polyphosphates is used in this process to prevent formation of deposits. $CaCO_3$ scale can be prevented in scale-forming water treated with only 0.5 mg/L of polyphosphate. The amount of polyphosphate required for effective scale control is far less than that required for complex formation on a stoichiometric basis, hence the name threshold treatment. Polyphosphates can hold iron (Fe) and manganese (Mn) ions in



$$\mathrm{Na-O-\overset{\overset{O}{\|}}{\underset{\underset{ONa}{\|}}{P}}-O-\overset{\overset{O}{\|}}{\underset{\underset{ONa}{\|}}{P}}-O-\overset{\overset{O}{\|}}{\underset{\underset{ONa}{\|}}{P}}-O-Na}$$

Figure 4.22 Polymer-like structure of tripolyphosphate.

solution in an environment where they would otherwise precipitate, for example, in the presence of oxygen or chlorine at pH over 8.

Polyphosphates are produced by dehydration of one or more orthophosphate (PO_4^{-3}) compounds. Using different mixtures of orthophosphates can vary the kinds of condensed phosphates formed. Condensed phosphates form chains containing the P – O – P group, as shown in Fig. 4.22 for tripolyphosphate. See Chap. 19 for more details on polyphosphates and other materials used to prevent scale and deposition.

Application of Water Chemistry

Several key aspects of water are critical for the water chemist or anyone working with water system operation in municipal, industrial, or institutional applications. These include an understanding of the actions of various cations in water, alkalinity and pH relationships, mineral solubility, and oxidation and reduction concepts. A water chemist or system operator must know how these dynamic factors affect the systems that use water.

Hardness and Analysis of Water

One common denominator in the majority of water problems is hardness, which is a folk term inherited from the past with its origins in household use of water for washing. In some places, surface or well waters were hard to use for the family laundry. More soap was needed to produce suds in these hard waters, and clothes would not be cleaned as desired. To improve this, many houses had a rain barrel or a cistern to collect soft rainwater for washing. Indeed, this relation between hardness and soap demand was so fundamental that a standard solution of soap was used for many years to determine the hardness of water. Thus, tradition defines hardness as the soap-consuming capacity of water. For practical purposes, hardness equals the calcium and magnesium content of water, although heavy metals such as iron and manganese also consume soap.

Hardness then, is the sum of calcium and magnesium cations in water, independent of the nature of the anions present. The quantity has traditionally been expressed in terms of calcium carbonate equivalents, that is, mg/L as $CaCO_3$. This is a fortuitous choice because the molecular weight of $CaCO_3$ is 100, and its equivalent weight is 50, providing a convenient unit for expressing all ions in water, rather than showing each with its own equivalent weight. Historically, water analyses reported all constituents using the calcium carbonate equivalent concept.

The practice of reporting all components as $CaCO_3$ equivalents is still a widely, but not universally, used form for reporting a water analysis. There are two other forms also used around the world: elemental concentrations, usually in mg/L or ppm; and equivalents per million (epm) or equivalents per liter (eq/L). Equivalents per liter are calculated by dividing the concentration of each ion in mg/L by the equivalent weight. Table 4.6 compares these three methods of reporting a water analysis.

Component	Concentration, (mg/L as Ion)	Concentration, epm or eq/L	Concentration, (mg/L as $CaCO_3$)
Calcium	46	2.30	115
Magnesium	14	1.15	57.7
Sodium	32	1.40	69.8
Potassium	2.7	0.07	3.5
Total cations	94.7	4.92	246
Bicarbonate	154	2.53	126
Sulfate	67	1.39	69.7
Chloride	34	0.96	47.9
Nitrate	3.6	0.06	2.9
Total anions	258.6	4.94	246.5
Total hardness		3.45	172.7
Total dissolved solids (TDS)	362		
Conductivity, µS/cm	483		
pH (pH units)	7.5		
Silica	8.3		
Iron	0.03		
Color, APHA* units	15		

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*American Public Health Association.

Table 4.6 Comparison of Water Analysis Reporting Methods on Mississippi River Water at Vicksburg, Mississippi

In the third column, the sum of all the anions determined by analysis is 4.94 epm. This slightly exceeds the total cations as determined by analysis (4.92 epm). Since the water must be electrically neutral, the sum of the cations should equal the sum of the anions; however, it is not unusual to find a modest discrepancy, because some minor constituents (perhaps ammonia, a cation) have not been reported, or because of limitations of individual ion tests.

Modern analytical methods make it easier to report the analyses in terms of elemental concentrations. These methods make possible the detection of many more components found in water. Nalco includes the concentrations of the major components like calcium, magnesium, alkalinity, sodium, and chloride reported in $CaCO_3$ equivalents. Compare the modern analysis of the Mississippi River shown in Fig. 4.23 to that in Table 4.6.

Wastewaters usually contain a number of ions that may not be shown in this illustration. Wastewater composition depends on the kind of plant operations through which the water has passed. For example, heavy metals such as zinc and copper may be present in waste from plating operations, organics are present in sewage treatment plant effluent, and fluoride may be present as an anion or an anionic complex in wastewater from glass manufacturing.

Alkalinity and pH Relationships

A working knowledge of the basics of pH and alkalinity relationships is necessary for any water system operation. The relationships between the forms of alkalinity as a function of pH can be determined with simple equations. This information can help diagnose problems with pH measurement equipment and as a check of whether a pH measurement is reasonable, based on the alkalinity.

The pH of Water

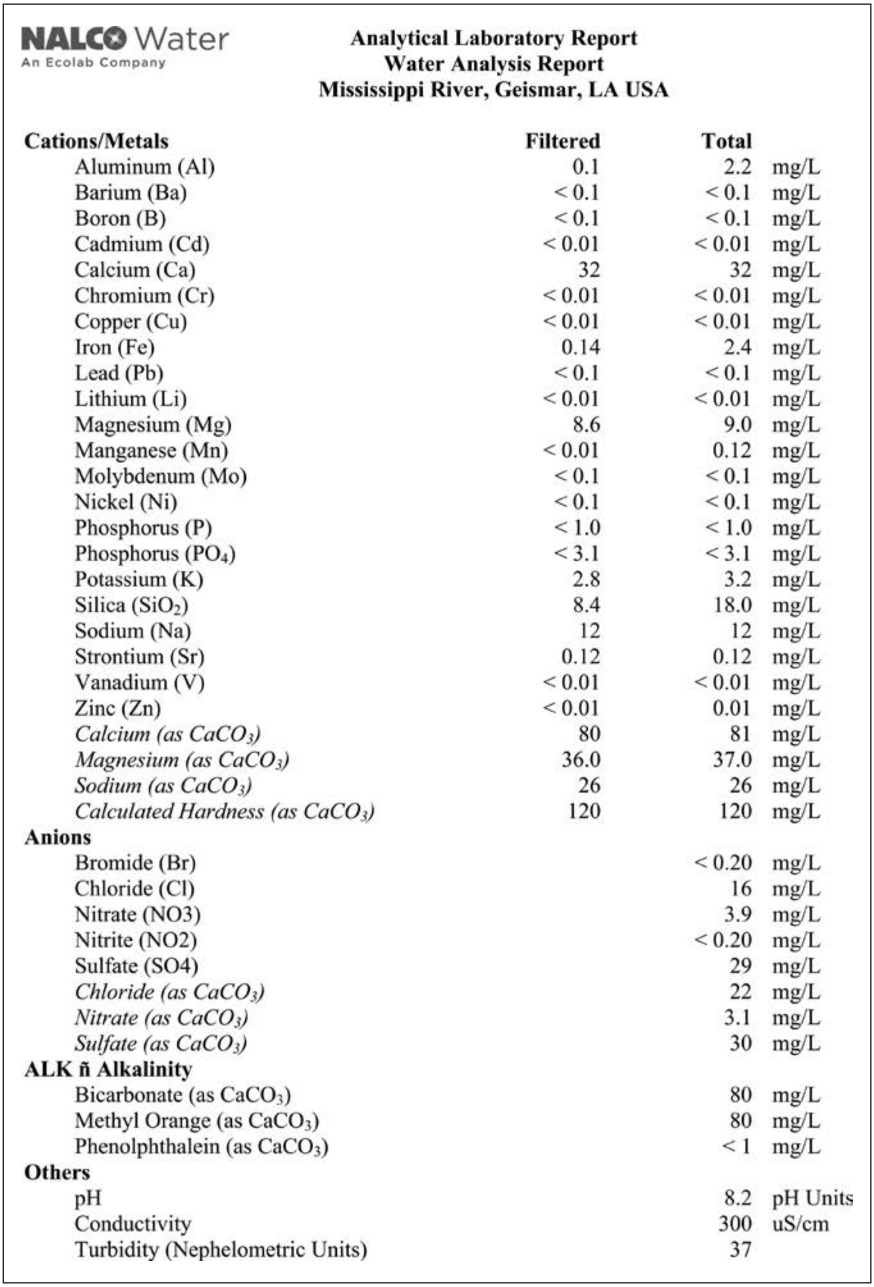
Certainly, pH is one of the most fundamental symbols for water treatment specialists. It is the convention used to specify given water along the range of acidity-alkalinity. A good understanding of the effect of pH on systems to be treated is valuable. Applying these concepts to the practice of water treatment is the objective.

The equilibrium reaction at the heart of an understanding of pH is the dissociation of the water molecule into hydrogen and hydroxyl (hydroxide) ions:

$$H_2O \leftrightarrow H^+ + OH^- \tag{4.17}$$

Dissociation of water into hydrogen and hydroxyl ions is governed by the dissociation constant in Eq. (4.18). This book will use the hydrogen ion (H^+) for simplicity rather than the more correct hydronium ion (H_3O^+).

$$K_w = [H^+][OH^-] = 10^{-14} \tag{4.18}$$



NALCO Water
An Ecolab Company

Analytical Laboratory Report
Water Analysis Report
Mississippi River, Geismar, LA USA

Cations/Metals	**Filtered**	**Total**	
Aluminum (Al)	0.1	2.2	mg/L
Barium (Ba)	< 0.1	< 0.1	mg/L
Boron (B)	< 0.1	< 0.1	mg/L
Cadmium (Cd)	< 0.01	< 0.01	mg/L
Calcium (Ca)	32	32	mg/L
Chromium (Cr)	< 0.01	< 0.01	mg/L
Copper (Cu)	< 0.01	< 0.01	mg/L
Iron (Fe)	0.14	2.4	mg/L
Lead (Pb)	< 0.1	< 0.1	mg/L
Lithium (Li)	< 0.01	< 0.01	mg/L
Magnesium (Mg)	8.6	9.0	mg/L
Manganese (Mn)	< 0.01	0.12	mg/L
Molybdenum (Mo)	< 0.1	< 0.1	mg/L
Nickel (Ni)	< 0.1	< 0.1	mg/L
Phosphorus (P)	< 1.0	< 1.0	mg/L
Phosphorus (PO_4)	< 3.1	< 3.1	mg/L
Potassium (K)	2.8	3.2	mg/L
Silica (SiO_2)	8.4	18.0	mg/L
Sodium (Na)	12	12	mg/L
Strontium (Sr)	0.12	0.12	mg/L
Vanadium (V)	< 0.01	< 0.01	mg/L
Zinc (Zn)	< 0.01	0.01	mg/L
Calcium (as $CaCO_3$)	80	81	mg/L
Magnesium (as $CaCO_3$)	36.0	37.0	mg/L
Sodium (as $CaCO_3$)	26	26	mg/L
Calculated Hardness (as $CaCO_3$)	120	120	mg/L
Anions			
Bromide (Br)		< 0.20	mg/L
Chloride (Cl)		16	mg/L
Nitrate (NO3)		3.9	mg/L
Nitrite (NO2)		< 0.20	mg/L
Sulfate (SO4)		29	mg/L
Chloride (as $CaCO_3$)		22	mg/L
Nitrate (as $CaCO_3$)		3.1	mg/L
Sulfate (as $CaCO_3$)		30	mg/L
ALK ñ Alkalinity			
Bicarbonate (as $CaCO_3$)		80	mg/L
Methyl Orange (as $CaCO_3$)		80	mg/L
Phenolphthalein (as $CaCO_3$)		< 1	mg/L
Others			
pH		8.2	pH Units
Conductivity		300	uS/cm
Turbidity (Nephelometric Units)		37	

Figure 4.23 Analysis of Mississippi River water using modern instrumental methods of analysis.

This means that as the hydrogen ion concentration decreases, the hydroxide ion concentration increases proportionally. At neutrality, where $[H^+]$ and $[OH^-]$ are equal, there are only 10^{-7} mol/L of each ion. This H^+ ion concentration equates to a concentration of only 0.005 mg/L as $CaCO_3$. Since dealing with such low concentrations is inconvenient, the pH scale was devised. The term pH is defined as the negative logarithm of the hydrogen ion concentration $[H^+]$:

$$\text{pH} = -\log[H^+] \tag{4.19}$$

The pH of 7.0, where both concentrations are equal, is the neutral point. Numbers below 7.0 indicate an increasing concentration of $[H^+]$ and thus an increase in acidity. Above 7.0, the $[OH^-]$ and hence the alkalinity is increasing. The pH scale is an indicator of the balance between hydrogen and hydroxide ions. It is not a quantitative measure of the level of acid or alkaline substances dissolved in water. Other ions like dissolved carbon dioxide, bicarbonate, and carbonate can affect the acidity or alkalinity of water. These materials affect the pH only to the extent that they liberate H^+ or OH^-.

The dissociation constant K_w changes with temperature and concentration of salts in the water. This must be taken into account when interpreting data involving pH. For example, many water applications operate at high temperature, and samples from the system are usually cooled before analysis. The H^+ and OH^- concentrations measured on the cooled sample, even though different from those in the hot system, are often used for control purposes. This practice can cause a system to operate at the wrong pH. Table 4.7 shows the variation of the pK_w ($-\log K_w$) as a function of temperature. Since K_w decreases as temperature increases, the pH of water decreases as it is heated to higher temperature (assuming no change in gas concentration, such as carbon dioxide).

Temperature, °F (°C)	pK_w
32 (0)	14.93
41 (5)	14.73
50 (10)	14.53
59 (15)	14.35
68 (20)	14.17
77 (25)	14.00
86 (30)	13.83
122 (50)	13.26

Table 4.7 Change of Dissociation Constant of Water versus Temperature

The hydrogen ion concentration can be measured with a pH meter. It can also be titrated, when the concentration becomes large enough to be detectable by chemical analysis. Since pH is a logarithmic function, the hydrogen ion concentration increases by a factor of 10 for each unit of pH reduction.

When the pH drops below approximately 5, the hydrogen ion begins to reach mg/L concentrations, enough to be determined by titration, using the correct organic dye indicator. The chemical indicator originally used for this purpose was methyl orange, changing color at pH 4.2 to 4.4. The color change of this indicator was so subtle that a new indicator was found to give a more pronounced color change. The new indicator produces a blue color on the alkaline side and red on the acid side, with gray at the endpoint. Even though this special indicator has replaced methyl orange, the measurement of total alkalinity by this titration is still called methyl orange alkalinity or M alkalinity. Total or M alkalinity exists above the approximate pH range of 4.2 to 4.4. Below this pH, free mineral acidity (FMA) exists. An approximate relationship between pH value and mineral acidity is shown in Table 4.8.

A pH meter can also determine the hydroxyl ion concentration, since the following relationships hold:

$$\mathrm{pOH} = 14 - \mathrm{pH} \tag{4.20}$$

$$\mathrm{pOH} = -\log[\mathrm{OH}^-] \tag{4.21}$$

When the pH of a water solution exceeds about 9.6 to 9.8, a measurable concentration of hydroxyl ions begins to appear. The hydroxyl

H^+, mg/L as $CaCO_3$	pH
2–3	4.3
4–5	4.0
6–7	3.9
8–9	3.8
10–11	3.7
12–13	3.6
14–16	3.5
17–20	3.4
21–25	3.3
31–40	3.1
41–50	3.0

Table 4.8 Mineral Acidity Shown as the Concentration of H^+ Ions versus pH

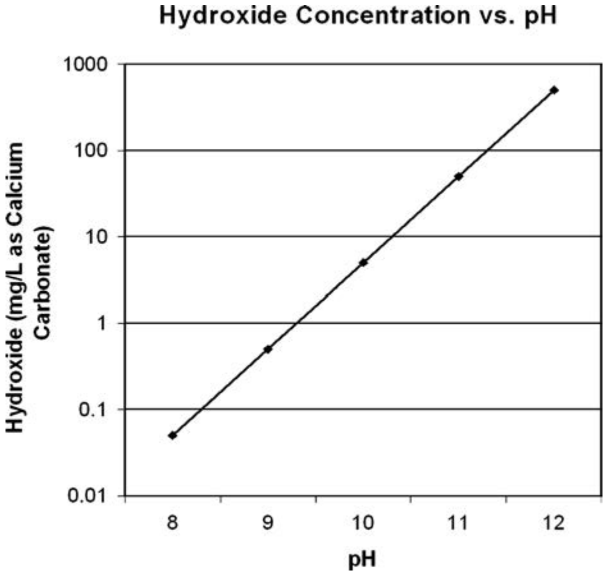


FIGURE 4.24 Concentration of hydroxide (in $CaCO_3$ equivalents) as a function of pH. Note that the hydroxide concentration is an insignificant part of alkalinity below pH 9.3.

alkalinity (caustic or OH^- alkalinity) can be determined either by using a pH meter or by titration. The relationship between hydroxyl alkalinity and pH is shown in Fig. 4.24. The hydroxyl ion does not have an appreciable effect on alkalinity until pH is above 9.3, where the OH^- concentration is above 1 mg/L as $CaCO_3$.

An understanding of these concepts is necessary to put these acidity-alkalinity relationships into perspective. To the theoretical chemist, a pH of 7 is considered neutral; to the water chemist, a pH of 7 in itself means very little. We must also know how much total alkalinity and how much free or combined CO_2 may be present. For the water chemist then, the dividing point between acidity and alkalinity is not pH 7.0, but rather the M alkalinity endpoint, corresponding to a pH of 4.2 to 4.4.

Another measure is P alkalinity (phenolphthalein alkalinity), which exists when the water is above pH 8.2 to 8.4. P alkalinity can be determined by titration with phenolphthalein indicator, which changes from pink or red above pH 8.4 to colorless below pH 8.2. In most natural water supplies, the pH is less than 8.2, and there is no P alkalinity. Very few natural waters have pH below about 5.0; strong mineral acids are seldom found in freshwater. The pH range between the M endpoint and the P endpoint defines the bicarbonate alkalinity range, where weak acids may be present, like carbonic acid.

Impact of Carbon Dioxide in Water

Dissolved carbonate salts in most natural water supplies, result from the action of carbon dioxide in water. At the normal atmospheric level of 0.04% CO_2, less than 1 mg/L CO_2 dissolves in rainwater. However, once rainwater penetrates soil, it is exposed to CO_2 gas levels much greater than in the atmosphere, created by respiration of soil organisms as they convert organic food into energy and CO_2. Well waters, which have percolated through this CO_2-rich zone, may contain from ten to several hundred mg/L dissolved CO_2. When CO_2 dissolves in water, it reacts with water to form carbonic acid, which dissociates into the hydrogen ion and the bicarbonate ion according to Eq. (4.4).

The reaction between acidic groundwater and limestone minerals is shown in Eq. (4.22). Magnesium and calcium are dissolved from a common mineral, dolomite [$CaMg(CO_3)_2$], to produce hardness and alkalinity in groundwater.

$$2H_2O + 2CO_2 + CaMg(CO_3)_2 \rightarrow Mg(HCO_3)_2 + Ca(HCO_3)_2 \qquad (4.22)$$

In most waters, some excess CO_2 remains dissolved in the water. This creates a balance between pH and alkalinity as shown in Fig. 4.25. The amount of dissolved CO_2 in water depends on the pH value and the alkalinity. The graph shows the ratio of carbon dioxide to total alkalinity as a function of pH. Since the amount of CO_2 given by Fig. 4.25 is proportional to total (M) alkalinity, water with 1 mg/L CO_2 and 10 mg/L alkalinity has the same pH as water with 10 mg/L CO_2 and 100 mg/L alkalinity. Both of these waters have a ratio of 1:10 for the concentration of CO_2 to total alkalinity. The water with 100 mg/L alkalinity has a greater buffering capacity, however.

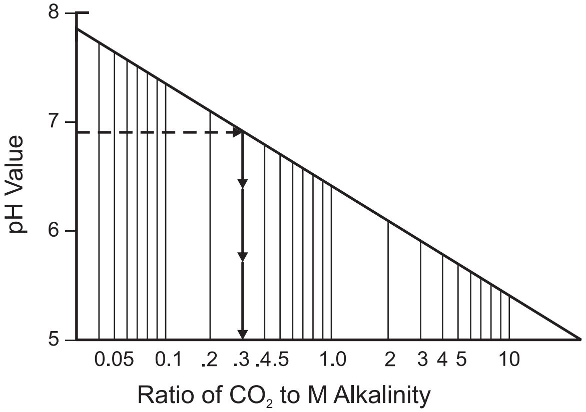


FIGURE 4.25 Approximate relationship of carbon dioxide, alkalinity, and pH in water. Both CO_2 and alkalinity are expressed in $CaCO_3$ equivalents.

If another 1 mg/L CO_2 were added to each water, the effect on pH would be greater in the first water with low CO_2 and alkalinity. The higher alkalinity in the second water moderates or buffers any pH change.

The graph in Fig. 4.25 can be used to determine the CO_2 concentration in water with a given pH and alkalinity. Using the example in Fig. 4.25, shown by the line with arrows, at pH 6.9, the ratio of CO_2 to total (M) alkalinity is 0.3. If the total alkalinity is 150 mg/L as $CaCO_3$, then the CO_2 concentration is 45 mg/L as $CaCO_3$. Using the conversion factor of 1.14, we can determine the carbon dioxide concentration as CO_2:

$$1.0 \text{ mg/L } CO_2 \text{ as } CO_2 = 1.14 \text{ mg/L } CO_2 \text{ as } CaCO_3 \tag{4.23}$$

Thus, 45 mg/L CO_2 as $CaCO_3$ is equal to 39.5 mg/L as CO_2. Note that this graph is limited to pH and alkalinity values where CO_2 is above a negligible concentration.

This demonstrates the balance between pH, alkalinity, and carbon dioxide in natural water. This balance depends upon a number of conditions, such as temperature, partial pressure of CO_2, and total alkalinity. Many well waters have a very high concentration of dissolved CO_2. In this case, even if the water has a high alkalinity, the pH is low. Figure 4.25 illustrates that as the ratio of CO_2 to total alkalinity increases, the pH of the water decreases.

It is essential to understand that this balance is affected by exchange of CO_2 between water and air. Under normal pressure, CO_2 establishes an equilibrium concentration in water, based on the pH and alkalinity of the water. Well water supersaturated with CO_2 loses carbon dioxide to the air when pumped out of the ground and exposed to lower pressure.

Distribution of Alkaline Species in Water

The relationship between pH, carbon dioxide, and alkalinity describes the general conditions of water, but it is still important to know the amount of individual alkalinity species in water. The equilibrium reactions and corresponding equilibrium constants for the carbonate system are:

$$H_2O + CO_2(\text{aq.}) \leftrightarrow H_2CO_3 \qquad K_H = 10^{-2.8} \quad \text{(Henry's Law)} \tag{4.24}$$

$$H_2CO_3 \leftrightarrow H^+ + HCO_3^- \qquad K_{a1} = 10^{-6.3} \tag{4.25}$$

$$HCO_3^- \leftrightarrow H^+ + CO_3^{-2} \qquad K_{a2} = 10^{-10.3} \tag{4.26}$$

From these equations, the fraction of inorganic carbon species as a function of pH can be determined as shown in Fig. 4.26.

Figure 4.26 shows that two inorganic carbon species exist between pH 4.3 and 12.3. Below pH 4.3, only CO_2 is significant, while above

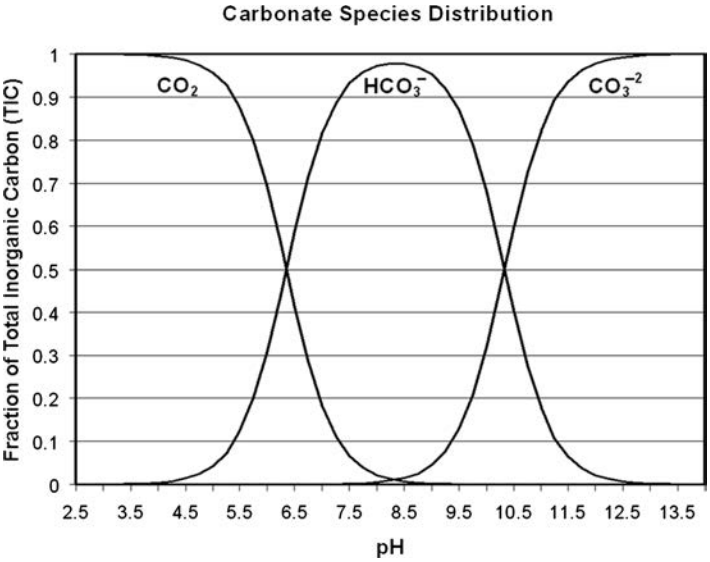


FIGURE 4.26 Fraction of inorganic carbon species versus pH.

pH 12.3, only CO_3^{-2} is significant. Below pH 8.3, only HCO_3^- and dissolved CO_2 exist in water. Above this pH, HCO_3^- and CO_3^{-2} are the predominant species. Of course, above pH 7, the OH^- concentration increases and contributes to alkalinity. The concentration of OH^- must be known to describe the alkalinity of water completely. As shown earlier in Fig. 4.24, OH^- does not have an appreciable effect on alkalinity until pH is above 9.3, where the OH^- concentration is above 1 mg/L as $CaCO_3$.

Using these relationships, along with titration measurements of alkalinity described earlier, three types of alkalinity can be defined:

1. Total or M alkalinity at the methyl orange end point (pH about 4.3)
2. P alkalinity at the phenolphthalein end point (pH about 8.3)
3. Hydrate or caustic alkalinity, which can be calculated from the other two

The ionic species represented by each type of alkalinity can be described as follows:

$$M = OH^- + HCO_3^- + CO_3^{-2} \tag{4.27}$$

$$P = OH^- + ½CO_3^{-2} \tag{4.28}$$

$$O = OH^- \tag{4.29}$$

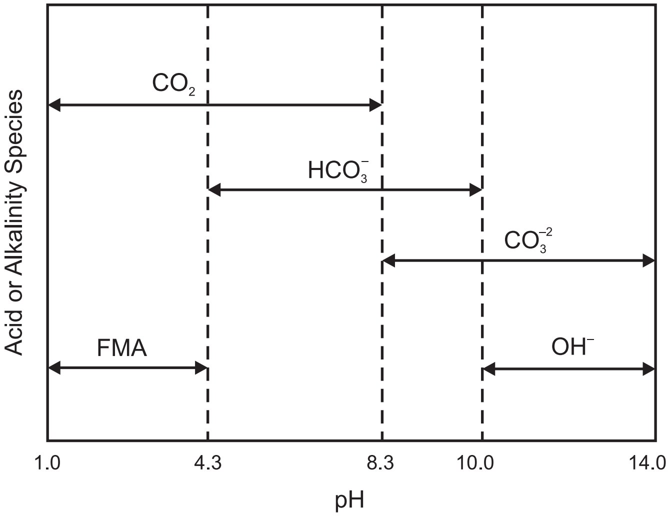


Figure 4.27 Simplified relationship between pH and alkalinity species.

These three equations are only valid when alkalinity is due to carbonate species hydroxide, and other species, like phosphate and ammonia, are negligible. Historically, this has been simply represented as shown in Fig. 4.27. In this diagram, some approximations have been made. The clear transition points are at pH 8.3, where carbonate is near zero, and at pH 4.3, where all alkalinity is near zero. However, two of the transitions shown at pH 10 are not so sharply defined. Figure 4.27 shows that bicarbonate exists above pH 10, and measurable quantities of OH^- exist between pH 9.2 and 10, although the concentration is very small. However, in the relationships shown in Fig. 4.27, both OH^- below pH 10 and HCO_3^- above pH 10 are considered negligible. These assumptions, although not strictly true, are commonly used as rules-of-thumb in the relationships that follow.

By definition, alkalinity ceases to exist at pH 4.2 to 4.4, and further reduction of pH produces free mineral acidity (FMA). Therefore, Fig. 4.27 leads to the following commonly used definitions and assumptions:

- Below pH 4.3, M = 0
- Below pH 8.3, $CO_3^{-2} = 0$
- Above pH 10, HCO_3^- is considered negligible
- Below pH 10, OH^- is considered negligible

Using the equations given above for the alkalinity species and these definitions from Fig. 4.27, a set of rules can be developed to determine

Result of Titration	OH^- as $CaCO_3$	CO_3^{-2} as $CaCO_3$	HCO_3^- as $CaCO_3$
P = 0	0	0	M
P < ½ M	0	2P	M-2P
P = ½ M	0	2P	0
P > ½ M	2P-M	2(M-P)	0
P = M	M	0	0

Table 4.9 Relationship between P and M Alkalinity and the Hydroxide, Carbonate, and Bicarbonate Concentrations in Water

the concentration of each species. The rules differ, depending on whether OH^- or HCO_3^- is present in measurable quantities. A complete set of these relationships can be developed, depending on the results of the M and P titrations (Table 4.9).

These approximations are very useful, but they may be subject to interferences, especially in contaminated waters where ammonia may be high. Wastewater may contain ions in addition to HCO_3^- and CO_3^{-2}, which are alkaline such as bisulfides, sulfides, and phosphates. Other ions like borate and silicate can affect alkalinity measurements. When dealing with such waters, M and P titrations are inadequate to determine HCO_3^- and CO_3^{-2} relationships; therefore, acid evolution of CO_2 must be used.

Remember that these are only approximations. For example, at pH 10, bicarbonate is set to zero, but it can be as much as 25% of the alkalinity based on Fig. 4.26. This practice tends to overstate carbonate alkalinity in the presence of OH^-. Therefore, these relationships work better as the pH of the system moves away from 10, either higher or lower. They remain convenient relationships that work reasonably well under most conditions encountered in water systems.

Buffer Capacity

A final consideration is the importance of the buffer effect of alkaline waters, a critical factor where careful control of pH may be necessary in treating either raw water or wastewater. As an example, compare the neutralization of sodium hydroxide (NaOH) to the neutralization of sodium carbonate (Na_2CO_3), as shown in Fig. 4.28. Control at pH 7 is virtually impossible in the NaOH neutralization, since there is a vertical drop between pH 9 and 4.3. Very little acid is required to change the pH from a value of 9 to 4.3 in water containing only NaOH. Controlling the addition of small amounts of acid and responding to a rapid pH change is very difficult. Water that is buffered with alkalinity (carbonate curve in Fig. 4.28) has a very gradual change in pH as more acid is added. This makes pH control in natural

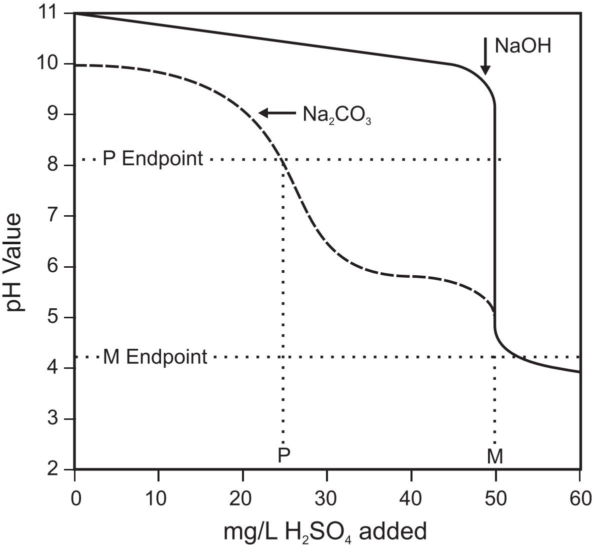


Figure 4.28 Neutralization with sulfuric acid (H_2SO_4) of alkaline water containing 50 mg/L alkalinity from either sodium hydroxide (NaOH) or sodium carbonate (Na_2CO_3).

waters (with typical alkalinity concentrations) much easier to accomplish than in unbuffered water. As a corollary to this, it is considerably easier to control the pH of an acidic waste with Na_2CO_3 than with NaOH, provided the CO_2 generation can be controlled without excessive foaming.

Practical Aspects of Mineral Solubility

Examination of acidity-alkalinity relationships in water reveals that the solubility of minerals such as calcium carbonate and magnesium hydroxide is more complicated to predict than the solubility product concept suggests. The numerous equilibrium reactions that describe calcium carbonate precipitation make this prediction difficult. For that reason, water chemists usually rely on empirical data based on reported plant experiences to estimate results of a precipitation reaction.

Solubility in Softening Reactions

Figure 4.29 shows data used for predicting calcium carbonate solubility, specifically related to precipitation in a lime softening operation. The difference in results between hot process softening [above approximately 212°F (100°C)] and cold process softening (ambient temperatures) is considerably beyond what would be predicted by simple solubility data, which show a decrease of only about 2 mg/L solubility at the higher temperature. The empirical

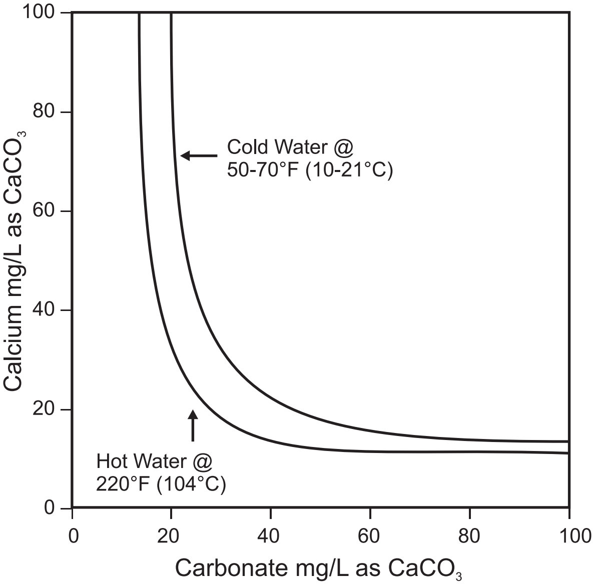


Figure 4.29 $CaCO_3$ solubility in hot and cold systems. (*Empirical data based on 60–90 min reaction and settling time.*)

temperature effect must be caused by other factors, such as rate of reaction, which approximately doubles for each 18°F (10°C) temperature increase, the nature of the precipitate (crystalline or amorphous), and the possible effect of coagulating organic materials at higher temperature.

Organic matter affects cold lime softening of municipal sewage, where residual calcium carbonate is invariably higher than when the same process is used in the treatment of freshwater. This is illustrated in Fig. 4.30. However, if sewage is heated above approximately 160°F (71°C), residual calcium carbonate after softening approaches that achieved in freshwater.

If magnesium precipitates with calcium carbonate, residual calcium in solution may be higher than if just calcium carbonate precipitates. Inclusion of other impurities, such as strontium, has been shown to increase solubility of calcium carbonate. Empirical data from a variety of plants should be used cautiously in estimating the results of lime treatment of an unknown water supply, especially if contamination levels are not fully defined. Actual bench testing to determine the response of that water to lime treatment is the best approach.

Magnesium solubility is as difficult to predict with accuracy as calcium solubility, for the same general reasons. The solubility of magnesium hydroxide is reported to be 30 to 40 mg/L at 77°F (25°C). Because of the difference in solubility product relationships,

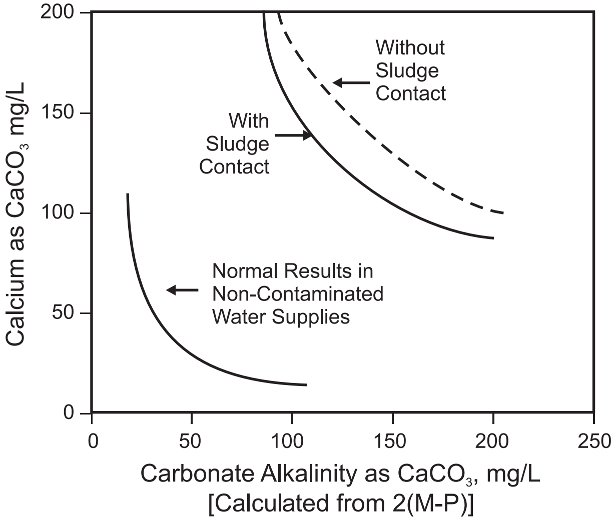


Figure 4.30 Cold lime softening of sewage (upper two curves) compared to raw water.

magnesium concentration is affected more by changes in hydroxyl concentration than calcium is by changes in carbonate concentration.

$$K_{Ca} = [Ca^{+2}][CO_3^{-2}] \tag{4.30}$$

$$K_{Mg} = [Mg^{+2}][OH^-]^2 \tag{4.31}$$

An increase in carbonate produces a corresponding decrease in calcium in Eq. (4.30). However, an increase in hydroxyl concentration affects the magnesium concentration in Eq. (4.31) in a squared relationship. Thus, a doubling of the $[OH^-]$ will result in the $[Mg^{+2}]$ to drop to one-fourth its original value.

When water is softened with lime, in the pH range of 9.5 to 10.5, magnesium precipitates as the hydroxide, and the precipitate is positively charged. In the same pH range, $CaCO_3$ precipitate is negatively charged. Furthermore, silica in the system is usually present as a strong negatively charged colloid. Sodium aluminate may be introduced in the system as a strong anionic complex. All of this may account for the coprecipitation of magnesium with calcium, the strong adsorption of silica on $Mg(OH)_2$ precipitate, and the low residual magnesium often achieved by the treatment of water with sodium aluminate in addition to lime.

In conventional softening operations, lime treatment of freshwater produces a $CaCO_3$ solubility of approximately 35 mg/L in cold water and 25 mg/L in hot water, and a residual magnesium hydroxide solubility of approximately 35 mg/L in cold and 2 to 3 mg/L in hot water.

Calcium carbonate and magnesium hydroxide are precipitated in the lime softening operation; however, these can precipitate from unstable water (water containing these materials in a supersaturated condition), if anything is done to the system to upset the equilibrium. The equilibrium shift could be caused by an increase in temperature, a decrease in pressure, turbulence, or contact with surfaces that seed the chemical precipitation. The most common product of instability of freshwater is $CaCO_3$; in seawater, the usual precipitate is $Mg(OH)_2$ or one of its complex carbonate-hydroxide salts.

$CaCO_3$ Stability Indexes

Historically, a variety of empirical and theoretical scaling index calculations have been used to predict the probability of mineral scale formation. Early methods of predicting the scale-forming tendency of water range from simple equilibrium saturation indexes to empirical indexes based on experimental or field data. The two key examples of these are the Langelier Saturation Index (LSI) and the Ryznar Stability Index (RSI).

These first indexes were an attempt to simplify the evaluation of the effect of water chemistry on scaling and corrosion in municipal drinking water systems. Both are based on calculations of the solubility of calcium carbonate, with minor corrections for temperature and ionic strength. These scaling indexes have many inherent limitations because of their simplified nature and do not consider all the complex factors in natural water that affect mineral solubility.

LSI was the first index calculation to come into wide usage (1920s). It is based on the saturation pH (pH_s), at which point a given water is saturated with calcium carbonate. LSI is determined by the difference between the actual pH and pH_s to define a saturation index:

$$\mathrm{LSI} = \mathrm{pH} - \mathrm{pH_s} \tag{4.32}$$

Positive LSI indicates the water solution is oversaturated with respect to calcium carbonate, while negative LSI indicates the water is undersaturated.

Based on studies of reported conditions of scaling and corrosion in a variety of municipal systems, Ryznar created an empirical index to predict scale-forming or corrosion tendency, based on pH and pH_s:

$$\mathrm{RSI} = 2\mathrm{pH_s} - \mathrm{pH} \tag{4.33}$$

A water solution is considered to be corrosive when the RSI exceeds approximately 6.0 and to be scale forming when the index is less than 6.0.

Other indexes, like the Stiff and Davis index, try to compensate for higher conductivity but are still limited in scope. None of these methods can consider all the factors in natural water that affect mineral solubility. The inherent limitations of these simplified indexes can give erroneous predictions of the scaling or corrosive tendency of water. The limitations of indexes are due to a variety of assumptions made in the calculations, including:

- The effects of temperature and ionic strength were either ignored or severely limited.
- The solubility of other scaling species (besides $CaCO_3$) was ignored.
- The effects of soluble complexes (ion pairing) were not calculated.
- A limited set of conditions was examined.
- Simplifying assumptions were made about the carbonate equilibria.

An example of the effect of ionic strength and ion pairing is illustrated by the difference between the predicted and actual solubility of $CaSO_4$ in a highly concentrated recirculating cooling water system (Fig. 4.31). The predicted solubility of Ca with increasing SO_4 concentration, shown by curve A, continues to decrease as conductivity increases. The actual solubility, in curve B, shows that a Ca concentration of 800 to 900 mg/L as $CaCO_3$ can be maintained, even at SO_4 concentrations in excess of 25 000 mg/L as $CaCO_3$.

Limitations of simple indexes are not due to lack of understanding of the problem, but rather to efforts to simplify the equations for

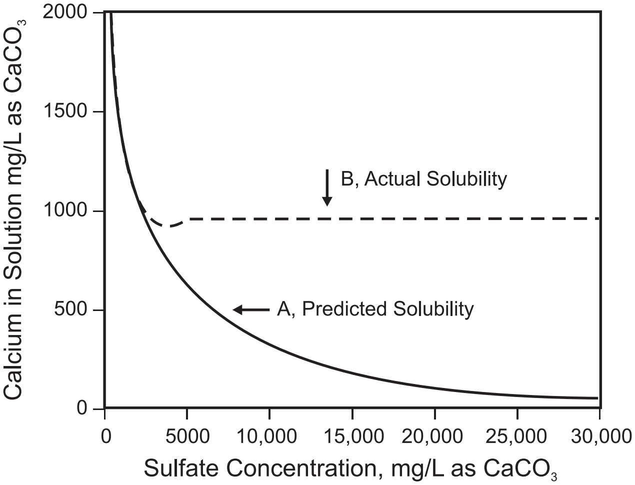


FIGURE 4.31 Effect of ionic strength on the solubility of $CaSO_4$ in highly concentrated cooling water.

easy use. Now, computer models that can run on any computer make rigorous calculations easily and quickly and include the effect of a wide variety of conditions. See Chap. 15 for more detail on models for solubility calculations.

Oxidation/Reduction Reactions

Oxidation and reduction reactions, also known as redox reactions, are important in water chemistry. A few examples of redox reactions include water disinfection, corrosion, precipitation of iron and manganese from water, and oxidation of sulfide for odor removal from water.

Basic Concepts

Redox reactions involve the transfer of electrons. In an oxidation reaction, electrons (e^-) are lost from a chemical reactant, like the oxidation of iron metal in corrosion, which releases two electrons:

$$Fe^\circ \rightarrow Fe^{+2} + 2e^- \qquad (4.34)$$

In this oxidation reaction, iron is an electron donor, and a reducing agent, since it supplies the electrons, which can reduce other reactants in water. This reaction is called a half-cell reaction, because the electrons must be accepted by another half-cell reaction. To maintain electrical neutrality, every oxidation reaction in a system must be accompanied by a reduction reaction. In this reduction reaction, another reactant gains the electrons donated by the reducing agent, as in the half-cell reaction below:

$$\tfrac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^- \qquad (4.35)$$

In this case, oxygen is an electron acceptor, and is reduced, since it gains the electrons. Oxygen can also be called an oxidizing agent or an oxidant. The two negative hydroxide ions produced in this reaction balance the positive charge on the ferrous ion (Fe^{+2}) to maintain neutrality.

These reactions should be familiar, since they are the corrosion reactions for iron-containing metals in water. They are called electrochemical reactions, since redox reactions involve the transfer of electrons. The power, or potential, of redox reactions can be determined from the electrochemical series (shown earlier in Table 4.2). In redox reactions, chemicals at the extremes of the series are more powerful oxidants or reductants. Sodium metal is a very strong reducing agent with a negative potential of –2.7 V. Fluorine is a very strong oxidizing agent with a positive potential of 2.87 V. There would be a very strong driving force for a reaction between sodium and fluorine.

Oxidizing or Reducing Conditions

Chlorine, bromine, and ozone are familiar in water chemistry as oxidizing biocides. They are applied to municipal water or treated sewage to kill pathogenic organisms; they control slime-forming bacteria and algae in cooling systems, clarifiers, and softeners.

Another important role for these chemicals is as oxidizing agents, especially for removal of iron and manganese from well water used for municipal water supply, and from acid mine drainage in coal producing regions. Iron and manganese are soluble in a reducing environment, such as deoxygenated well water, and found as the ferrous (Fe^{+2}) and manganous (Mn^{+2}) ions. Oxidation to ferric (Fe^{+3}) and manganic (Mn^{+4}) ions reduces solubility substantially.

Redox potential is measured using a pH instrument with special electrodes. In the absence of a redox electrode in field-testing, there are several simple methods for qualitatively judging the redox state. The following can identify a reducing condition:

- Sulfide may be present; the sample may have a sulfide odor or may react to lead acetate paper (turn white lead acetate paper black).
- The color of methylene blue indicator disappears.
- A test for oxygen is negative.
- Test for presence of reducing agent is positive, such as the boiler water test for sulfite, using the same method.

Similarly, an oxidizing condition is indicated by a few conditions:

- Color of methylene blue dye persists.
- Oxygen test is positive.

Common Oxidizing and Reducing Agents

Although chlorine or hypochlorite is most frequently chosen as the oxidizing agent, it is not always the best. Table 4.10 shows a listing of various available oxidizing agents and their comparable oxidizing powers. Sometimes, the chemistry of the aqueous environment rules out the use of chlorine, as in the case of water high in ammonia, which consumes the chlorine to produce chloramines (still an oxidizer but weaker than chlorine). Oxidizing agents like permanganate, chlorine dioxide, and ozone are not affected by ammonia, and are better oxidants in this case.

Some heavy metals are best removed by reduction. Mercury salts can be reduced to mercury metal by strong reducing agents like the borohydrides and then filtered from solution. When metals have been oxidized (or reduced) to an insoluble form, most become colloidal particles and are then removed from water by coagulation, flocculation, and filtration. If the metal concentration

Element or Compound	Half-Cell Reactions	Standard Electrode Potential (V)
Oxygen (in neutral water)	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	0.40
Oxygen (acidic)	$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	0.68
Hypobromite	$OBr^- + H_2O + 2e^- \rightarrow Br^- + 2OH^-$	0.76
Hydrogen peroxide (basic)	$H_2O_2 + 2e^- \rightarrow 2OH^-$	0.87
Hypochlorite	$OCl^- + H_2O + 2e^- \rightarrow Cl^- + 2OH^-$	0.89
Bromine	$Br_2 + 2e^- \rightarrow 2Br^-$	1.08
Ozone (basic)	$O_3 + H_2O + 2e^- \rightarrow O_2 + 2OH^-$	1.24
Chlorine	$Cl_2 + 2e^- \rightarrow 2Cl^-$	1.36
Permanganate (acidic)	$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$	1.68
Hydrogen peroxide (acidic)	$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	1.77
Ozone (acidic)	$O_3 + 2H^+ + 2e^- \rightarrow O_2 + H_2O$	2.07
Fluorine	$F_2 + 2e^- \rightarrow 2F^-$	2.87

TABLE 4.10 Table of Standard Electrode Potentials for Common Oxidizing Agents. Oxidation Potential Increases as the Potential Becomes More Positive

is over 2 to 5 mg/L, sedimentation is included before filtration to avoid rapid plugging of the filter.

Oxidation-reduction reactions can be very slow, especially compared to acid-base neutralization reactions, which are essentially instantaneous. Solution pH is important because it influences solubility and reaction rates. Oxidation reactions of iron and manganese are faster at high pH, when an oxidizing agent can increase the potential of the water. Therefore, at pH 5, a large detention basin is usually needed to provide time for these oxidation reactions; at pH 8.3 to 8.5, iron can be oxidized in-line and filtered with less than five minutes contact time with an oxidant. Certain materials catalyze the rate of oxidation. Fortunately, MnO_2 is such a catalyst, easily applied as potassium permanganate ($KMnO_4$), which also acts as an oxidant.

CHAPTER 5

Impurities in Water

Contaminants in water sources are related to rainfall, the geologic nature of the watershed or underground aquifer, biological activity in the ground or in the water, and the activities of human population. As described in the previous chapter, many contaminants are due to the unique solvent properties of water. The electrical polarity of the water molecule aids dissolution of many ionic and covalent compounds. Substances like salts, sugars, acids, and alkalis are very soluble in water. Many gases, including oxygen (O_2) and nitrogen (N_2), are soluble in water. Other gases that dissolve in water, like carbon dioxide (CO_2) and ammonia (NH_3), react with the water molecule to form weak acids or bases. Polar organic materials, like alcohols and sugars, dissolve in water to a high extent, depending on the properties of the molecule. The presence of polar organics in water can act as a cosolvent to dissolve small amounts of nonpolar organic compounds. The action of biological processes in water can increase or decrease the solubility of inorganic and organic materials in water.

The density and viscosity properties of water, combined with the power of flowing water, can keep in suspension, a wide variety of materials. These suspended particles can be inorganic solids, insoluble organic substances, or biological organisms.

Water supports all life forms known on Earth. The solvent properties allow fluids like blood to carry nutrients to the cells in a body. Water participates in many metabolic processes necessary for life. An example is photosynthesis, where energy from the sun is used by plants to convert CO_2 and water into sugar.

The result is that water can contain many substances, both living and nonliving. The materials in water may be either inert or reactive. The specific type of contaminant and its concentration depends upon the type and source of water. Understanding the various contaminants that can be found is the first step in water treatment for any use, from potable water to industrial applications.

The goal of this chapter is to present various impurities found in water and their effect on industrial processes. This is not an exhaustive list of impurities but includes many that are commonly found.

Characteristics of Water Sources

Chapter 2 on Water Sources and Stressors provided many examples of ground and surface water sources around the world. The rivers and lakes described in that chapter are typical of waters used for industrial purposes as well as for municipal drinking water. However, other sources of water are used for industrial and institutional purposes. Reclaimed wastewater is sometimes used and creates additional challenges, depending on contaminants remaining in the water, the particular industry, and the intended use of the water. Seawater may be used in a variety of applications and is commonly used for cooling in power utilities in coastal areas. Each source has an individual chemical composition that is specific to the nature of the source and the surrounding area, yet there are several general characteristics of water sources that are unique to each type of water.

One of the key factors that affect the quality of water is the geological nature of the area where the groundwater or surface water exists. Surface water composition is affected by contact with the soil or rock of the watershed that supplies either a river or lake. Groundwaters are dependent on the type of rock through which rainwater permeates when entering the aquifer. In addition, CO_2 created by the action of bacteria in soil, and absorbed from air by rainwater, can make water slightly acidic. If subsurface rock contains limestone, groundwater in that area can be high in hardness (calcium and magnesium) and alkalinity. General characteristics of some of the main sources of water used for industrial and institutional processes are shown in Table 5.1.

In addition, there are some general differences between groundwater and surface water. Many of these properties are direct opposites. Groundwater typically has these characteristics:

- Temperature remains constant throughout the year.
- Dissolved solids concentration is generally higher than surface water at the same locale. Groundwaters are often high in hardness and alkalinity, if those minerals are present in the substrate. In some areas, salt water or connate water (water trapped underground) intrusion may add considerable amounts of sodium chloride and other salts. Some areas overlie underground soda ash (sodium carbonate) formations; these waters contain very high levels of sodium and alkalinity but very little hardness.

Source of Water	Chemical Content	Potential Positives of the Water Source	Potential Negatives of the Water Source
Municipal drinking water	Ranges from very soft with low conductivity to very hard with high conductivity.	Generally, good quality with low bacterial counts and free of suspended solids.	Often the costliest source. Surface water may have seasonal variation, or groundwater may be very hard. Aluminum or iron carryover is possible, depending on clarification method.
Surface water from rivers	Generally, lower in hardness than groundwater, depending on the geographic area of the source.	Large rivers can provide consistent water quality with only filtration or clarification needed for pretreatment.	Water chemistry, biological contamination, and suspended solids vary seasonally. Heavy rain can increase suspended solids and microbial deposits. Agricultural runoff areas may add phosphate or nitrate. Chloride varies in estuaries based on seasonal and tidal fluctuations.
Surface water from lakes	Generally, lower in hardness and more constant than groundwater.	Variability may be low, particularly with large lakes. Water chemistry can be good. May be very low in suspended solids.	Contaminants vary seasonally. Concentration can occur over time in smaller lakes. Seasonal inversion can raise potentially anaerobic water from the lake bottom. Algal blooms in summer can occur.
Groundwater	Ranges from very soft with low conductivity to very hard with high conductivity.	Generally consistent, with little variation of water chemistry, temperature, biological population, or suspended material.	Often the hardest water source, with high calcium hardness and alkalinity. Other problems can be ionic content as high as 5000 mg/L, high silica, anaerobic bacteria, soluble iron, soluble manganese, and hydrogen sulfide (H_2S).

Table 5.1 Types and Characteristics of Water Sources

Source of Water	Chemical Content	Potential Positives of the Water Source	Potential Negatives of the Water Source
Process wastewater or gray water	May have contaminants or increased ion concentration from the process where water was used.	A potential low-cost source. Environmentally proactive, particularly in arid areas.	Contaminants present may increase corrosion and fouling. Compared to a primary water source, it may contain higher organics, have variable pH, or high suspended solids. May require pretreatment or use of equalization tank to minimize variability.
Municipal sewage plant effluent	Contains varying contaminants, organics, or increased concentration of some ions.	A potential low-cost source. Incentives may be provided to promote use. Environmentally proactive, particularly in arid areas.	Often contains phosphate, nitrogen compounds, organics, biological organisms, and higher chloride and sulfate than freshwater in the same area. Requires additional pretreatment such as lime softening to reduce hardness, alkalinity, and phosphate, or biological treatment to remove organics, ammonia, and phosphate.

TABLE 5.1 Types and Characteristics of Water Sources (*Continued*)

- Dissolved gases such as hydrogen sulfide (H_2S) and CO_2 may be present in well water at levels above saturation. Both gases can cause the water to be corrosive. When the water is brought to atmospheric pressure, these gases can be released. When CO_2 is released, the resulting pH increase of the water may cause scale formation. Release of H_2S can cause odor problems in the area surrounding the water source.
- Alkalinity and pH remain constant in groundwater. The water can be highly acidic (pH as low as 4.3) or very alkaline (pH as high as 9.8) depending on the minerals present.
- Metal ions like iron and manganese are often present as soluble ions in groundwater sources. They may be oxidized to insoluble forms after the water contacts air.
- In most cases, turbidity of groundwater is generally very low.

Surface water quality is not generally as uniform as groundwater. In fact, the variability of surface water can be a challenge for industrial water treatment applications.

- Temperature can vary seasonally but also in much shorter periods, depending on conditions upstream from point of use. Temperature and weather changes can cause inversion of a lake, where water from the bottom of the lake is raised to the lake surface. Lake bottom water can contain anaerobic bacteria and high levels of iron and manganese.
- Total dissolved solids (TDS) are generally lower than in groundwater. Depending on other industrial processes located upstream, there might be significant variability.
- Dissolved gases are present because the water is continuously in contact with air; however, excess dissolved gases are not generally present.
- Alkalinity and pH vary seasonally due to precipitation and runoff. There can be geographic variations in the TDS, pH, and various contaminants from discharge of municipal waste, industrial waste, or farm runoff into the river or lake.
- Metal ions may be present in surface water supplies because of industrial pollution. Most metals in surface waters are commonly present as insoluble particulate metal oxides. In some cases, the soluble form may be present.
- Suspended solids and turbidity in surface water can be high, particularly in rivers, and varies seasonally with rainfall and runoff. Rapid changes are possible, depending on upstream or climatic events.

Classes of Impurities

There are many ways to group impurities found in water sources, most of which are arbitrary classifications. Impurities can be grouped by different ranges of concentrations, by ranges of the solubility of the materials, or by type of material, such as inorganic and organic compounds. The most common way is probably to group matter by whether it dissolves in water (soluble) or whether it is not soluble in water (insoluble). However, even with this classification, further breakdown or special groups are probably needed. For example, many gases dissolve in water and may have significant interaction with other species in water, because the gases like CO_2 or NH_3 may react with water. Organic compounds should be in a separate category, because even low concentrations of some organics can cause serious problems in many industrial systems or are health hazards in drinking water, whether they are soluble or insoluble. Biological growth, such as bacteria, algae, or macroorganisms, should also be a separate category, due to the complex nature of these living creatures and the by-products they release.

In this chapter, grouping the impurities as follows allows a logical discussion of each group of materials and their effect on industrial systems:

- Soluble matter
- Insoluble matter (suspended material)
- Organic contaminants
- Biological contaminants
- Dissolved gases
- Radioactive materials

The variety of materials in this list show the complexity of water-based systems and the challenges that are involved when using natural water in industrial, institutional, or municipal water systems.

Dissolved Substances

Dissolved substances can be found at very high concentrations, like sodium and chloride in ocean waters, or as trace components, like selenium and titanium. The components may be completely dissolved and soluble in the source water but become insoluble when used in an industrial or institutional process. Insolubility may be caused by temperature and ion concentration changes in the process where the water is used. Solubility of various ions is governed primarily by the solubility product constant for any compound that may form. The solubility of carbonate with various positive ions is

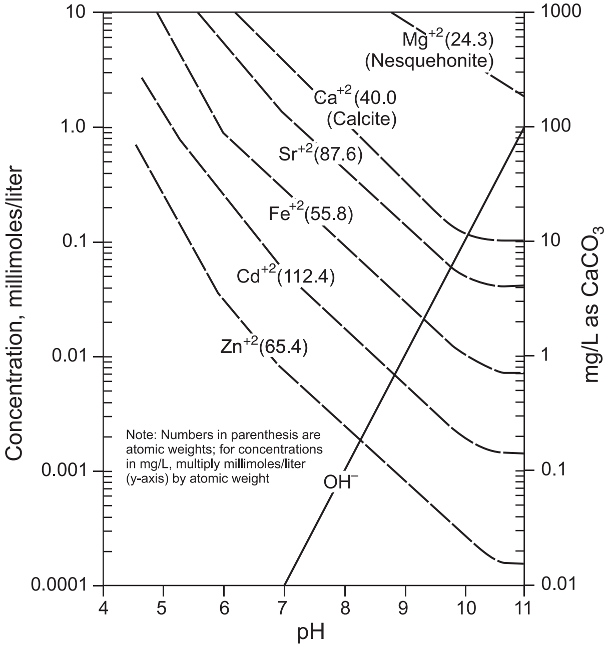


FIGURE 5.1 Theoretical solubility of carbonate compounds in a water system closed to an external CO_2 environment. (*Source: Stumm and Morgan, 1970.*)

shown in Fig. 5.1. Examples of the solubility of various hydroxide and oxide compounds are shown in Fig. 5.2. However, many other processes, like common-ion effects or ion pairing, can affect solubility of a mineral. Therefore, the prediction of mineral solubility in an industrial or institutional process is not a simple matter that can be calculated by common indexes. (See Chap. 15 on Cooling Water Deposition for more detail on factors affecting solubility in cooling water systems.)

TDS is the sum of all materials dissolved in water and is usually in the range of 25 to 5000 mg/L. The suggested limit for public water supplies, based on potability, is 500 mg/L. The principal effect of dissolved solids on industrial processes is to limit the extent to which water can be concentrated before it must be discarded. High concentrations can cause scale formation, affect the taste of beverages, or cause other problems depending on the manufacturing process. The related electrical conductivity of high TDS tends to accelerate corrosion. The conductivity of water can be used as a relative indicator of TDS.

Dissolved matter in water can be present as a compound like ethanol or as dissolved ions from a mineral or salt. These dissolved ions can be divided into two groups based on concentration. The

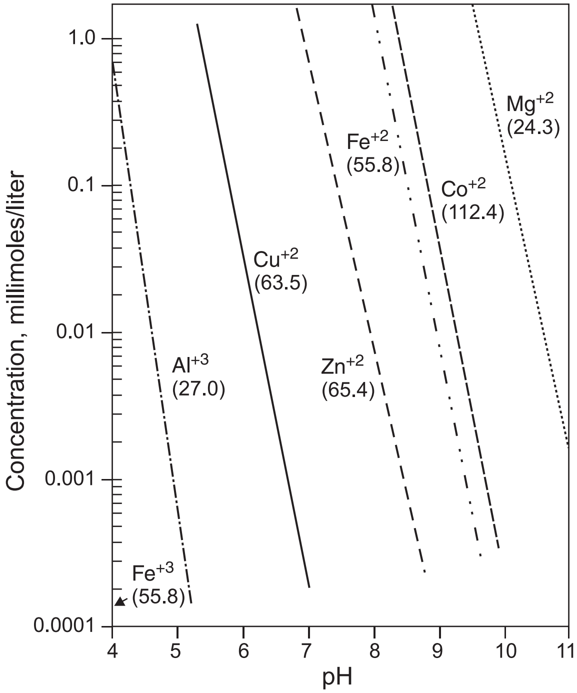


FIGURE 5.2 Theoretical solubility of oxides and hydroxides in water at 25°C. (*Source: Stumm and Morgan, 1970.*)

major constituents that are generally present in high concentration (>5 mg/L) are shown in Table 5.2.

Bicarbonate (HCO_3^-)

The bicarbonate ion is the principal alkaline constituent of almost all water supplies. Bicarbonate concentration is generally 5 to 500 mg/L as calcium carbonate ($CaCO_3$). One cause of bicarbonate in natural water is the presence of limestone rock in the watershed or subterranean rock. Normal activities of the human population introduce alkaline materials into water, evidenced by a typical increase of alkalinity of sewage plant effluent of 100 to 150 mg/L above the alkalinity of the municipal water supply. Much of this is due to the alkalinity of industrial and domestic detergents. Alkalinity in drinking water supplies seldom exceeds 300 mg/L. Control of alkalinity is important in many industrial applications, because of its significance in calcium carbonate scale formation. Alkalinity control is important in both concentrated boiler water and cooling water in evaporative cooling systems. Makeup water for these systems must often be pretreated for alkalinity reduction, or by direct acid addition. Alkalinity is objectionable in certain other industries, such as the beverage industry, where it neutralizes the

Species	Impact on System Operation
Calcium	Forms various insoluble calcium scales. Higher concentrations are indicative of greater scale forming tendency.
Magnesium	Most magnesium-based minerals are more soluble than calcium salts but can be problems in some processes like seawater evaporators. Magnesium silicate can occur at alkaline pH when water contains silica.
Bicarbonate (Alkalinity)	Provides buffer capacity due to carbonates and bicarbonates. The potential for calcium carbonate scale formation can be determined primarily with the alkalinity, pH, and calcium concentration.
Chloride	A soluble anion that is aggressive to most metals. Higher concentration generally indicates higher corrosion potential.
Silica	Silica can form hard scale in some systems. Silica is more soluble as the pH increases; however, magnesium silicate can precipitate as the pH increases above 8. The silicate that forms at high pH contributes to measured alkalinity.
Sulfate	An anion that is reasonably soluble and can increase the corrosion potential at higher concentrations. Can form calcium sulfate scale at higher sulfate concentration, especially if calcium is greater than 800 mg/L as $CaCO_3$.

Table 5.2 Major Components That Affect Water Chemistry

acidity of fruit flavors; and in textile operations, where it interferes with acid dyeing.

Total alkalinity (also called M alkalinity) is a measure of all titratable species that neutralize acid. If the relationship between pH and alkalinity is outside the norm, M alkalinity may include other species besides bicarbonate and carbonate, like phosphate, silicate, or ammonia.

Calcium (Ca^{+2})

Calcium is the major component of hardness in water and usually is in the range of 5 to 500 mg/L as $CaCO_3$ (2–200 mg/L as Ca). Calcium, along with alkalinity, is a major factor in determining the scale forming or corrosive tendency of water. It is present in many minerals, principally limestone and gypsum. Limestone deposits are often the residues of the fossils of tiny aquatic organisms, such as polyps, that have taken calcium from seawater in which they lived and used it for their skeletons. This is but one of many cycles in nature whereby some component of the environment is continually withdrawn by living things and eventually returned directly or indirectly.

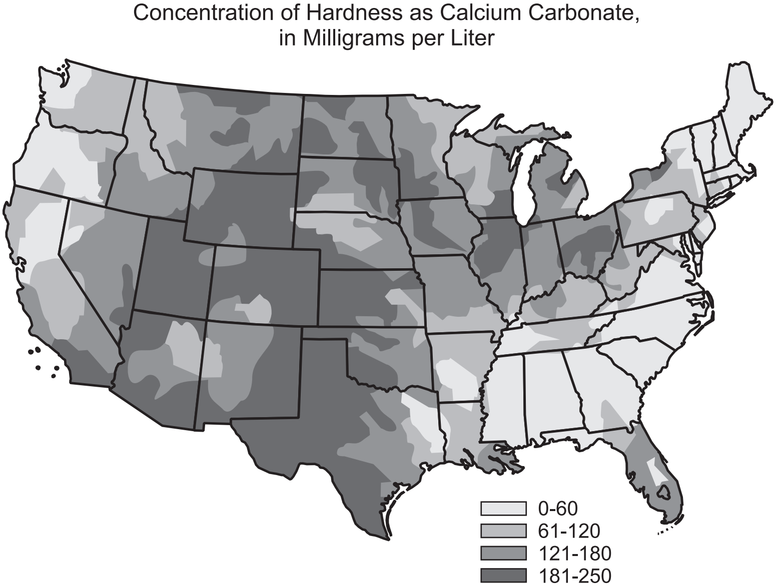


Figure 5.3 The calcium hardness of water can vary significantly depending on location because of the minerals in the soil that contact groundwater or surface water. (*Adapted from content provided by the United States Geological Survey*.)

Chloride (Cl^-)

Since almost all chloride salts are highly soluble in water, chloride is common in freshwater supplies, ranging from 10 to 100 mg/L. Seawater contains over 30 000 mg/L as sodium chloride (NaCl), and certain underground brine wells may actually be saturated (approximately 25% NaCl). Many geologic formations were once sedimentary rocks in the sea, and it is not surprising they contain residues of chlorides that are continually leaching into freshwater sources. The chloride content of sewage can be 200 mg/L above the concentration of the municipal water supply, accounting in part for the gradual increase in salinity of rivers as they proceed from headwaters to the sea. The recommended upper limit for chloride in drinking water is 250 mg/L, based entirely on taste, not on any known physiological hazards.

Magnesium (Mg^{+2})

The magnesium hardness of water is usually about one-third of the total hardness, the remaining two-thirds being calcium hardness. Magnesium typically ranges from about 40 to 200 mg/L as $CaCO_3$ (10–50 mg/L as Mg). In seawater, the magnesium concentration is about five times that of calcium on an equivalent basis. The production of magnesium hydroxide from seawater is the starting point in the manufacture of magnesium. Magnesium is a prominent component of many minerals, including dolomite, magnesite, and numerous varieties of clay.

Since magnesium carbonate is appreciably more soluble than calcium carbonate, magnesium is seldom a major component in scale, except where silicate is present in the water or in seawater evaporators. However, magnesium must be removed along with calcium, where soft water is required for boiler makeup or for process applications.

Silica (SiO_2)

Silica is present in almost all minerals, and is found in freshwater at 1 to 100 mg/L as SiO_2. The skeletons of diatoms are pure silica, and the silica content of surface waters may be affected by seasonal diatom blooms. Silica may be dissolved, but is often colloidal because of its reaction with adsorbents like magnesium oxide (MgO) and ferric hydroxide [$Fe(OH)_3$], thereby having characteristics similar to typical colloids. There is probably equilibrium between the silica in colloidal form and the bisilicate ($HSiO_3^-$) anion. Because of this complexity, it is difficult to predict the solubility of silica as water concentrates by evaporation.

The term "colloidal silica" is loosely used by water chemists and can be confusing. Small polymeric silica chains can form in solution. Larger polymeric groups may not be measured when analyzing

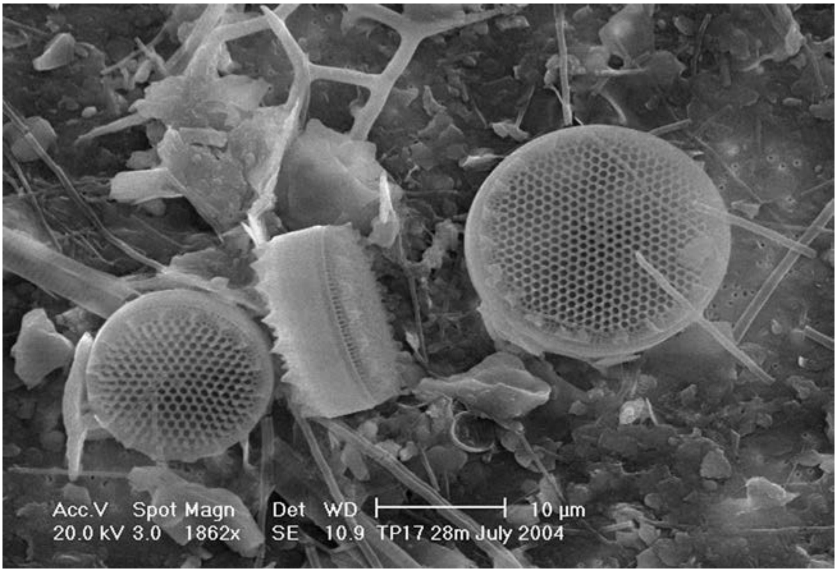


Figure 5.4 Diatoms create a skeleton of silica as seen by a scanning electron microscope (CC BY-SA 4.0, via Wikimedia Commons.)

dissolved silica by the typical molybdate-reactive method. The undetected silica may be termed colloidal silica. A more accurate statement would be that inert (or nonreactive) silica is present, since most of the silica is colloidal, although of differing sizes. Silica is objectionable at high concentration in cooling tower makeup because of this uncertainty about its solubility limits.

Silica is objectionable in boiler feedwater makeup because it may form scale in the boiler itself, and because it volatilizes at high temperatures and redeposits on turbine blades. Treatment processes that remove silica include adsorption on magnesium precipitates in lime softening, adsorption on ferric hydroxide in coagulation processes using iron salts, anion exchange in the demineralization process, and reverse osmosis (RO).

Sodium (Na^+)

Sodium salts are highly soluble in water, although certain complexes in minerals are not. The high chloride content of brines and seawater is usually associated with the sodium ion. In freshwaters, its range is usually about 20 to 200 mg/L as $CaCO_3$ (10–100 mg/L as Na). Sodium is present in certain types of clay and feldspar. There is an increase of sodium in municipal sewage of 40 to 70 mg/L in excess of the municipal water supply. Its concentration is not limited by federal drinking water standards, and persons on low sodium diets may require special sources of potable water.

Sulfate (SO_4^{-2})

Sulfate dissolves in water from certain minerals, especially gypsum, or appears from the oxidation of sulfide minerals. It's typical range is 5 to 200 mg/L as SO_4. The suggested upper limit in potable water is 250 mg/L, based on taste and its potential cathartic effect. Because calcium sulfate is relatively insoluble (<2000 mg/L), sulfate may be objectionable in water concentrating processes that are high in calcium, as in an evaporative system.

Aluminum (Al^{+3})

Although aluminum constitutes a high percentage of the earth's crust as a common component of a wide variety of minerals and clays, its solubility in water is so low that it is seldom a cause for concern in either municipal supplies or industrial water systems. However, in industrial systems, the carryover of alum floc from a clarifier may cause deposit problems, particularly in cooling systems where phosphate is used for corrosion control. Aluminum found in treated water systems is usually due to colloidal residues of alumina (Al_2O_3) from coagulation of water, when alum or sodium aluminate is used as the coagulant. If the residuals are objectionable, they can be removed by improved filtration practices.

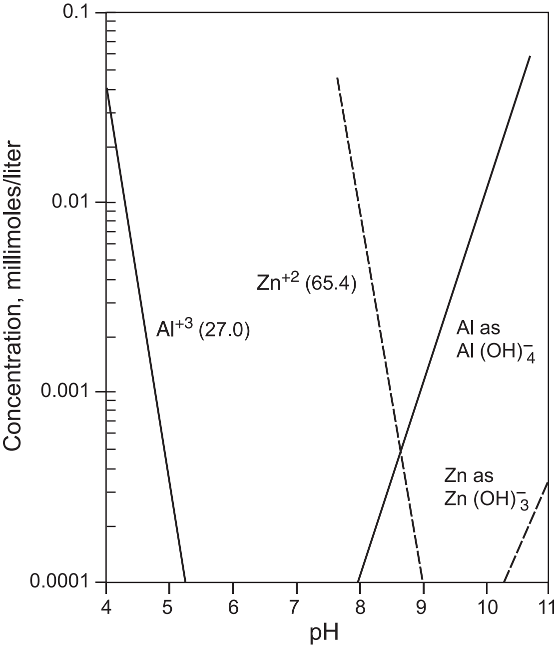


Figure 5.5 Theoretical solubility of aluminum and zinc in water at 25°C, showing the amphoteric nature of both metal ions. (*Source: Stumm and Morgan, 1970.*)

As shown by the solubility curves (Fig. 5.5), aluminum is amphoteric, meaning soluble at both low and high pH. In water, soluble aluminum is present as Al^{+3} or lower valence hydroxyl forms at low pH and the aluminate anion [$Al(OH)_4^-$] at higher pH values. As might be expected from this amphoteric nature, alumina particles are positively charged at low pH and negatively charged at high pH, as indicated by Fig. 5.6. The effectiveness of alum in precipitating negatively charged colloids, such as clay particles from water, is more likely related to the charge on the precipitated alumina than the charge on the aluminum ion itself, since the aluminum ion is not soluble in the typical coagulation pH of 5 to 7. Its strong negative charge at pH 10.0 to 10.5 helps explain the effectiveness of sodium aluminate in precipitating magnesium hardness, which is positively charged at this pH.

Arsenic (As)

The solubility of arsenic in water is so low that its presence is usually an indicator of either mining or metallurgical operations in the watershed or runoff from agricultural areas, where arsenical materials have been used as industrial poisons. If in colloidal form, it would be removed by conventional water treatment processes. Federal

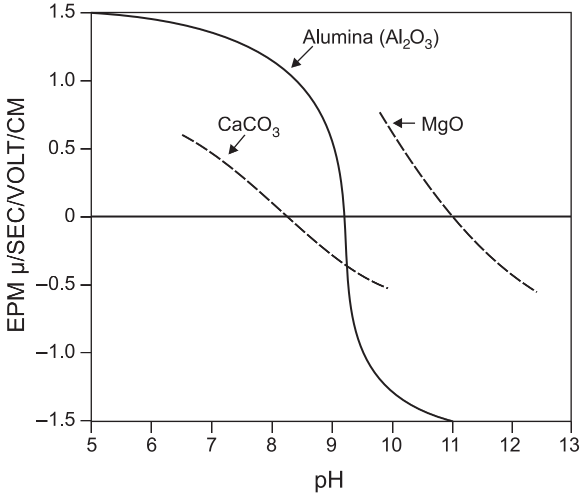


Figure 5.6 Variation of particle charge with particle type and solution pH. (*Source: Stumm and Morgan, 1970.*)

regulations limit the content in public water supplies to 0.01 mg/L total arsenic. If the material is present in organic form, it may be removed by oxidation of the organic material and subsequent coagulation or by an adsorption process, such as passage through granular activated carbon.

Barium (Ba^{+2})

In natural waters containing bicarbonate and sulfate, the solubility of barium is less than 0.1 mg/L as Ba, and it is seldom found at concentrations exceeding 0.05 mg/L. Removal to low residuals can be expected in conventional lime treatment processes. There are instances of barium being added to water for the specific purpose of sulfate reduction. The reaction is hindered because the barium reagent itself is so insoluble that considerable time is needed for the reactions to occur; furthermore, sulfate deposition on the surface of the barium reagent makes the process inefficient. Barium is limited in drinking water to a maximum concentration of 2 mg/L.

Borate [$B(OH)_4^-$]

Most of the world's boron is contained in seawater at 5 mg/L as B. Pure supplies of sodium borate occur in arid regions where inland seas evaporated to dryness, especially in volcanic areas. Boron is frequently present in freshwater supplies from these same geologic areas. It is present in water as nonionized boric acid [$B(OH)_3$]. At high pH (>10), most of it is present as the borate anion [$B(OH)_4^-$]. Borate is used for pH adjustment and buffering in closed cooling systems. Its concentration is not limited in municipal waters by potable water standards.

Borate can be damaging to citrus crops if present in irrigation water, and irrigation methods tend to concentrate the material in the soil. Although boron is in the same group on the periodic chart as aluminum, it behaves more like silica in aqueous systems.

Bromide (Br^-)

Bromine is found in seawater at about 65 mg/L as the bromide ion; some connate waters produced with oil contain several hundred milligrams per liter and are the source of commercial bromine. Over 0.05 mg/L in freshwater may indicate the presence of industrial wastes, possibly from the use of bromo-organo compounds such as biocides or pesticides.

Copper (Cu^+ and Cu^{+2})

Copper may be present in water from contact with copper-bearing minerals or mineral wastes from copper production. It is more likely, however, copper found in water is a product of corrosion of copper or copper alloy piping or fittings, or may have been added deliberately as copper sulfate to a water supply reservoir for algae control. When copper sulfate is added for algae control, because its solubility is limited, organic chelating materials may be added to the copper sulfate formulation to keep the copper from precipitating, and therefore maintain its effectiveness. Drinking water regulations limit the municipal water supply concentration to 1 mg/L. At higher concentrations, the water has an astringent taste. If a water supply is corrosive to copper, the first drawing or tapping of the supply from piping, which has been idle overnight, may contain relatively high concentrations, and ingestion of this water may cause immediate vomiting. In industrial supplies, the presence of copper can be objectionable, as it is corrosive to aluminum. Copper is essential to certain aquatic organisms, being present in hemocyanin in shellfish, the equivalent of hemoglobin in humans.

Fluoride (F^-)

Fluoride is a common constituent of many minerals, including apatite and mica. It is common practice to add fluoride to municipal water to provide a residual of 1.5 to 2.5 mg/L as F, which is beneficial for control of dental caries. Concentrations above approximately 5 mg/L are detrimental, however, usually causing mottled, brittle tooth structure. Because of this, the concentration is limited by drinking water standards to 4 mg/L. High concentrations are present in wastewaters from glass manufacture, steel manufacture, and foundry operations. Lime precipitation can reduce this to 10 to 20 mg/L.

Iron (Fe^{+2} and Fe^{+3})

Iron is found in many igneous rocks and in clay minerals. In the absence of oxygen, iron is quite soluble in the reduced state, which is the ferrous form (Fe^{+2}). This can be seen in an analysis of well water containing iron. When oxidized to ferric ion (Fe^{+3}) at pH 7 to 9, iron is insoluble, and the concentration can be readily reduced to less than 0.3 mg/L as Fe, the suggested maximum set by drinking water standards. Because iron is so insoluble when oxidized completely, the actual residual iron after treatment is determined by how well the colloidal iron has been coagulated and filtered from the water. Because iron is a product of corrosion in steel piping systems, iron found in water from a distribution system is often from the pipes and does not represent iron left from the treatment process in the water treatment plant.

Lead (Pb^{+2})

The presence of lead in freshwater usually indicates contamination from metallurgical wastes or from lead-containing industrial poisons, such as lead arsenate. However, lead may appear in water because of corrosion of lead-bearing alloys, such as solder. Being amphoteric, lead is attacked in the presence of caustic alkalinity.

The limitation on lead in drinking water is 0.015 mg/L as Pb, which should be readily achieved with good filtration practice. In wastewaters where lead may be complexed with organic matter, it may be solubilized, and oxidation of the organic may be required for complete lead removal.

Lithium (Li^{+})

This alkaline earth element is rare in nature and seldom analyzed in water. There are no records of experience indicating that this material is of concern either in industrial or municipal water supplies. However, lithium salts are used in psychotherapy to combat depression, so there may be a concentration level in water that has a psychotropic effect. Lithium salts have a wide variety of uses, but the industrial consumption is so low that it is not likely to be a significant factor in wastewaters.

Manganese (Mn^{+2}, Mn^{+4})

Manganese is present in many soils and sediments as well as in metamorphic rocks. In water free of oxygen, it is readily dissolved in the manganous (Mn^{+2}) state and may be found in deep well waters at concentrations as high as 2 to 3 mg/L as Mn. It is also found with iron in acid mine drainage. Wastewaters from metallurgical and mining operations frequently contain manganese. It is an elusive material to deal with because of the great variety of complexes it can form depending on the oxidation state, pH, bicarbonate-carbonate-hydroxide equilibria, and the presence of other materials, particularly iron. The suggested drinking water limit is 0.05 mg/L, because higher concentrations cause manganese deposits and staining of plumbing fixtures and clothing. However, even lower concentrations can cause similar effects, as it may accumulate in the distribution system as a deposit, to be released in higher concentrations later if the environment changes, such as by change in pH, CO_2 content, oxidation potential, or alkalinity. In industrial systems, it is as objectionable as iron, particularly in textile manufacture or the manufacture of bleached pulp, since small amounts of deposited manganese can slough off to stain products, which must be rejected. Certain textile finishing operations require reduction to levels as low as 0.01 mg/L.

In the oxidized manganic (Mn^{+4}) state, manganese is insoluble. Organic materials can chelate manganese much as they chelate iron and increase its solubility. Because manganese accumulates in sediments, it is common to find high levels of manganese in deep water, where none may be apparent at the surface. This should be studied in designing the proper intake structure for a plant water supply. An example of this is illustrated in Fig. 5.7, showing hypothetical manganese concentrations in a lake at various times of the year and at different depths.

Nitrate (NO_3^-)

Nitrate, like ammonia, comes into water via the nitrogen cycle, rather than through dissolving minerals. Its concentration is limited

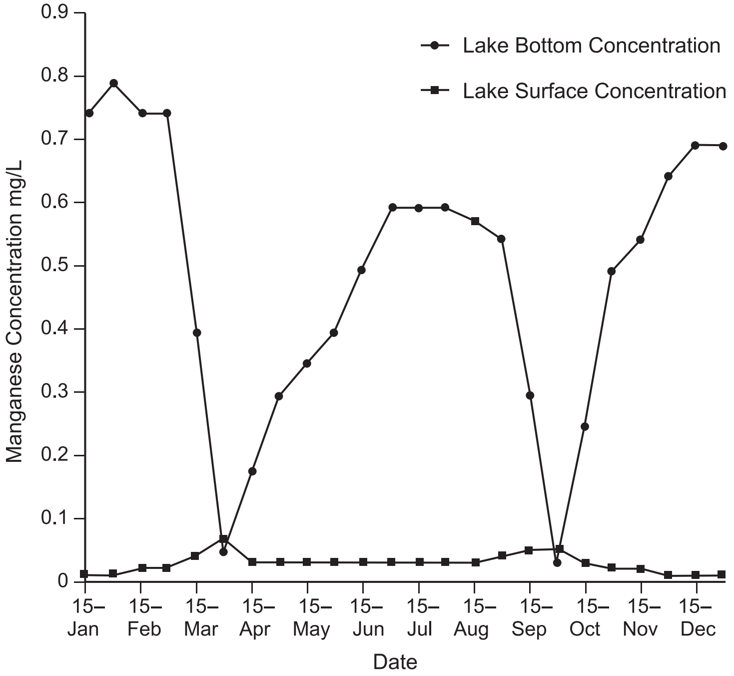


Figure 5.7 Hypothetical example of seasonal inversion of a lake that is 93 ft (28 m) deep. The soluble manganese concentration varies significantly at the bottom, but only slightly in the oxygenated surface layers of water.

by drinking water standards to 10 mg/L as N for physiological reasons. There are no reported uses of water where nitrate is a restrictive factor. Total nitrogen in sewage plant effluent can increase 20 to 40 mg/L as N above the level in the municipal water supply. Sources of this nitrogen include nitrate and ammonia. Nitrate can be converted to nitrogen in a biological system by the action of nitrifying bacteria. The nitrate content of well water may be higher than surface water, unless the surface water is contaminated with agricultural fertilizers.

Phosphate (PO_4^{-3})

Phosphorus is found in many common minerals such as apatite, in the form of orthophosphate (PO_4^{-3}). Since phosphate compounds are widely used in fertilizers and detergents, it is common to find phosphate in silt from agricultural runoff, with high concentrations being found in municipal wastewater, generally in the range of 5 to 15 mg/L as PO_4, but it can be as high as 15 to 30 mg/L as PO_4. Since phosphate is a primary cause of excessive algal growths, which lead to eutrophication of lakes and streams, legislated reduction of phosphate from all sources continues in many parts of the world.

Phosphate may be present in water as HPO_4^{-2} and $H_2PO_4^-$ as well as the higher pH form PO_4^{-3}. The distribution as affected by pH is shown in Fig. 5.8. Phosphate can be reduced to very low levels by treatment with alum, sodium aluminate, or ferric chloride, which causes formation of insoluble aluminum phosphate or iron phosphate. It can also be precipitated with lime at pH > 10 to produce residuals less than 2 to 3 mg/L in the form of hydroxyapatite; in a hot process system, the

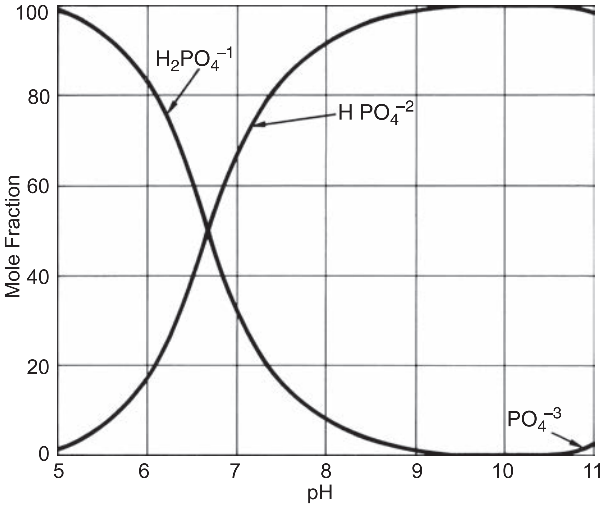


FIGURE 5.8 Effect of pH on the distribution of phosphate ions in solution.

residuals would be less than 0.5 mg/L. These phosphate precipitates are often colloidal, and filtration is required to achieve low residuals.

Potassium (K^+)

Potassium is closely related to sodium, so much so that it is seldom analyzed as a separate constituent in water analysis. Its occurrence is less widespread in nature, and for that reason, it is found at lower concentrations than sodium. It has no significance in public water supplies or in water used for industrial purposes. As with sodium, it can be removed chemically only by cation exchange or by physical processes such as evaporation and reverse osmosis. Potassium salts are highly soluble in water, but as a common constituent of clays, potassium is kept from dissolving by the nature of the structure of clay. For that reason, when water-formed deposits contain significant levels of potassium, it is probably caused by silt, in which case the deposit would also be high in Al_2O_3 and SiO_2.

Strontium (Sr^{+2})

Strontium is in the same family as calcium, magnesium, and barium and has low solubility in the presence of bicarbonate (about half that of calcium). Strontium is only found in areas of geologic formations where lead ores occur, and therefore its concentration in water is typically quite low. It is completely removed by any process used for calcium removal. If not removed by softening, in scale-forming water, it is a contributor to the scale problem.

Zinc (Zn^{+2})

Zinc is a metal, behaving quite like calcium in solution, although zinc has considerably lower solubility than calcium in natural waters with a neutral pH and bicarbonate alkalinity. Figure 5.5, shown earlier, illustrates zinc solubility characteristics. Zinc is seldom found at concentrations over 1 mg/L as Zn, with a typical concentration being approximately 0.05 mg/L. Because it tends to have an astringent taste, its concentration in public water supplies is recommended as 5 mg/L maximum.

Zinc may be present in water because of waste discharges from mining, metallurgical, or metal finishing operations. It may also appear because of corrosion of galvanized steel. Zinc is often included in proprietary corrosion inhibitors, where its effect on steel piping is similar to that of galvanizing.

Suspended Matter

A variety of matter can be suspended in water, particularly flowing water. Silt, sand, and soil are perhaps the first things that one thinks of as suspended matter in water. Pictures of the great rivers of the world illustrate the brownish, muddy appearance of the water. Aerial photos of the mouth of the Amazon River in Brazil show suspended matter carried for long distances out into the Atlantic Ocean by the powerful flow of the river. While most of the suspended matter in rivers is probably soil removed from the drainage basin, other suspended matter can be organics and metal ions. Decaying organic material, bacteria, algae, protozoa, etc. can all contribute to suspended matter in natural waters. In the open oceans, plankton is the major component of suspended material. Metal ions such as iron and manganese in their oxidized states can contribute to suspended matter in water. While these metal ions are soluble in many groundwater sources, iron and manganese are insoluble metal oxides present in particulate form in oxygenated waters.

Lake water can contain suspended material, depending on the characteristics of the body of water. Generally, lake water has much lower suspended solids than river waters. A young lake in a mountainous region, with a rocky bottom, may be very clear and have less than 1 mg/L suspended matter. An older lake, which has significant bottom sediment, can have higher suspended solids content, partly consisting of biological organisms. Seasonal turnover in lakes can temporarily increase the suspended solids concentration.

While suspended particles in water are not true colloids (like milk), colloidal properties help to keep the particles suspended in the water. Electrostatic forces between particles can determine whether particles repel each other or are attracted to each other. In most cases, particles in water have a natural, negative charge on the surface. This electrical charge serves to repel other like particles when two or more particles interact. Another force that affects particle interaction is the van der Waals force, which is a weak, short-range, attractive force. The fluctuating negative charge on a particle surface can create a temporary dipole moment in a particle. This dipole can induce another opposite dipole in a nearby particle. In this case, the particles are attracted to each other. These surface charges are the basis for the functioning of both dispersant and coagulation technology. Anything that increases or reinforces the surface charge helps keep the particles suspended, while anything that neutralizes the surface charge causes the particles to agglomerate and settle out of solution.

Organic Matter (Carbon, C^{+4})

Since organic material makes up a significant part of the soil and because it is used by aquatic organisms to build their bodies and produce food, it is inevitable that water-soluble organic products of metabolism should be present in all water supplies. Analytical data on the many organic compounds in most water sources are not generally available. Therefore, indexes such as those described in Table 5.3 are used. There are literally hundreds of thousands of known organic compounds, many of which might find their way into the hydrologic cycle. Methods of analysis exist for organic materials of interest,

Test	Description
BOD	Biochemical oxygen demand measures the ability of common bacteria to digest organic matter, usually in a five-day incubation at 20°C, by analyzing depletion of oxygen. This measures biodegradable organic matter, expressed as mg/L O_2.
COD	Chemical oxygen demand measures the ability of hot chromic acid solution to oxidize organic matter. This analyzes both biodegradable and nonbiodegradable (refractory) organic matter, expressed as mg/L O_2.
Color	Color is a rough measure of tannin, lignin, and other humic matter in surface waters and certain wastes, such as Kraft pulping wastes. Reported in American Public Health Association (APHA) color units related to cobalt and platinum standards.
DOC	Dissolved organic carbon is a measure of the total dissolved organic matter in water. The sample is filtered through a 0.45 μm or 0.22 μm membrane to remove undissolved organics, then acidified, and purged to remove inorganic carbon. Analysis by TOC follows, reported as mg/L C.
Solvent extractables	Extractables measures the organic matter directly extractable from water, using an organic solvent, usually hexane (C_6H_{14}), although carbon tetrachloride (CCl_4) and chloroform ($CHCl_3$) may be used. Reported as mg/L.
TOC	Total organic carbon measures the CO_2 produced from organics, when a water sample is atomized into a combustion chamber. The CO_2 equivalent to the alkalinity may be removed first, or this equivalent may be subtracted from the total CO_2 to determine organic carbon. Reported as mg/L C.

Table 5.3 Commonly Used Methods for Determination of Organic Matter in Water

especially those considered toxic or carcinogenic, such as polychlorinated biphenyls (PCB) and absorbable organic halogen (AOX). In general, indirect measures of organics in water are used instead. Examples include biochemical oxygen demand (BOD), chemical oxygen demand (COD), and total organic carbon (TOC).

Many waters have a yellowish or tea color due to decayed vegetation leached from the watershed by runoff. These organic materials are broadly classified as humic substances, further categorized as humic acid (a water-soluble compound), fulvic acid (alkali-soluble material), and humin (high molecular weight, water-insoluble matter). These organic compounds are molecules having many functional groups containing oxygen and hydrogen atoms in various proportions, so that when organic matter is reported as carbon, as in TOC determination, it is probable that the molecular weight of these humic organic molecules is 2.0 to 2.5 times greater than the value reported as carbon. A survey of 80 municipal supplies in the United States showed an average TOC content in the finished water of 2.2 mg/L as C, and the organic matter was probably about 5 mg/L.

Organic matter in a river can vary significantly over the length of the river. Figure 5.9 shows the dissolved organic carbon (DOC) along the length of the Mississippi River. DOC is a measure of the total dissolved organic matter. Most organic matter is from natural sources, and wastewater contributes small amounts of DOC. The concentration of DOC is dependent on volume and flow of the river, as evidenced by decreasing concentration downriver near New Orleans. Absorbable organic halogen (AOX) is a measure of halogenated organics dissolved in water. Some AOX may be natural, but many AOX compounds result from chlorination or bromination of water, including drinking water, wastewater before discharge, and process applications that require bleaching, such as in the paper industry. AOX compounds may be volatile or nonvolatile, and some may be toxic. The concentration of AOX along the Mississippi River varies significantly, but in no specific pattern, along the length of the river (Fig. 5.9).

Because some of the functional groups in humic compounds have ion exchange properties, they tend to form soluble complexes with heavy metals. In spite of this, there is no correlation whatever between the color of water and its total heavy metal concentration.

A study of the Rhine River showed that humic substances comprised from 25% at 1000 m^3/s to 42% at 3500 m^3/s of the dissolved organic matter; sulfonic acids ranged from 41% at 1000 m^3/s to 17% at 3500 m^3/s; a third category, chloro-organics, ranged from 12% at low flow to 5% at high flow. Chloro-organics are refractory, or nonbiodegradable classes of organic matter. The significance of this information is simply that each investigator selects the most practical categories to study and the simplest methods of analysis. There is usually no purpose in identifying 30 to 40 specific organic compounds in water (a rather costly procedure), if rough indexes such as TOC or DOC suffice for the study.

Some organic materials are truly soluble, but many, like humic matter, are colloidal and can generally be removed by coagulation (Fig. 5.10). Alum coagulation at pH 5.5 to 6.0 typically reduces color to less than five APHA units. Organic matter found in domestic sewage often inhibits calcium carbonate precipitation. If natural color exceeds about 50 APHA units, it must be partially removed for lime softening to occur. Organic matter may be removed by activated carbon treatment, which is widely practiced in municipal treatment plants when organic matter causes objectionable tastes or odors in the finished water.

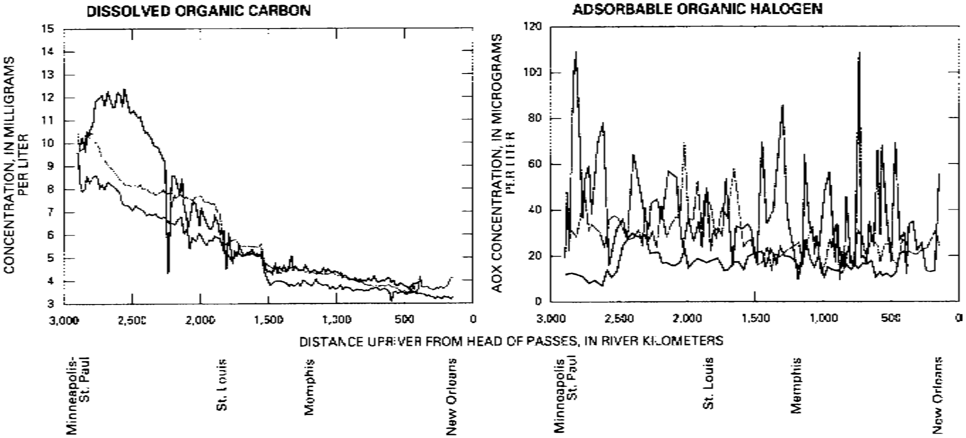


Figure 5.9 Dissolved organic carbon and absorbable organic halogen along the Mississippi River. (*Source: Figure 54 in USGS Circular 1133, 1995; Courtesy of the U.S. Geological Survey*.)

Figure 5.10 A clarifier can effectively remove the majority of suspended solids and humic matter from raw water as illustrated by the output water.

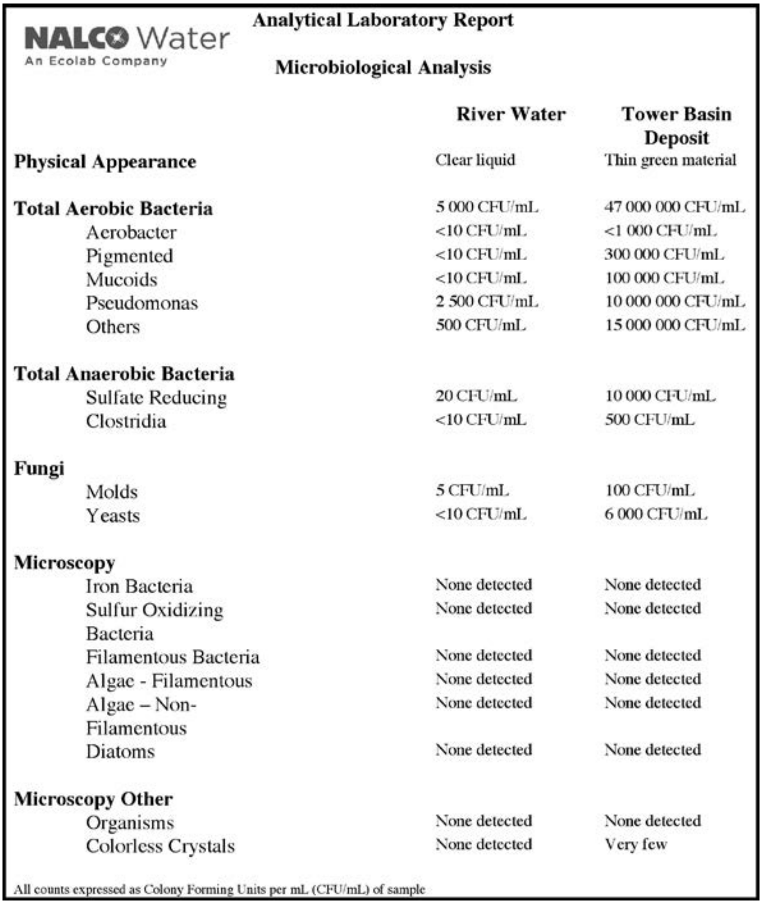
Generally, these tastes and odors are produced by algae, each species having its characteristic odor or taste just as with land plants. Like land plants, algae produce organic compounds, and may be toxic if enough is ingested by fish or animals. Organic matter is objectionable in municipal water chiefly for aesthetic reasons. It can be troublesome in industrial supplies by interfering with treatment processes. It is a major factor in the fouling of anion exchange resins, degrading effluent quality of demineralized water, and requiring early replacement of resin.

Many organic compounds found in nature are the result of human activity and carried by wastewater discharge into bodies of water. For example, caffeine can be found in rivers (ng/L concentrations) below municipal wastewater plant discharges. Pharmaceutical compounds have been found at very low levels in lakes and rivers. Certain organic materials in water polluted by agricultural runoff (eg, pesticide residues) or by industrial wastes in concentrations below 1 mg/L can exert a significant effect on the biota of the receiving stream. Even when the effect is not dramatic, such as a fish kill, it may have long-term consequences, such as affecting reproduction or disrupting the food chain.

Biological Organisms

Water is essential for life and there are many organisms, large and small, that make their home in water. Generally, microorganisms are considered troublesome contaminants in either drinking water or industrial water. However, several macroorganisms like zebra mussels can cause trouble for systems that use water directly from rivers or lakes. Describing all organisms that may be troublesome in systems that use water is beyond the scope of this book. Therefore, only an introduction to biological organisms is presented. Other chapters have details on organisms for biological digestion of wastewater, cooling water biological fouling, and pathogenic organisms like *Legionella*.

Microbial analyses are conducted to pinpoint problems in domestic and industrial water systems. There are thousands of species of microbes, and a variety of methods exists to identify troublesome organisms. The most common is the plate count, where bacteria from a water sample are grown on special types of agar containing nutrients specific to different species. The result of the plate count is a number of organisms per volume of sample. Bacteria, fungi, and molds can be determined by plate count methods. Other organisms like algae, iron-depositing bacteria, and protozoa may be identified visually by microscopic inspection. Figure 5.11 illustrates analyses



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Analytical Laboratory Report

Microbiological Analysis

	River Water	**Tower Basin Deposit**
Physical Appearance	Clear liquid	Thin green material
Total Aerobic Bacteria	5 000 CFU/mL	47 000 000 CFU/mL
Aerobacter	<10 CFU/mL	<1 000 CFU/mL
Pigmented	<10 CFU/mL	300 000 CFU/mL
Mucoids	<10 CFU/mL	100 000 CFU/mL
Pseudomonas	2 500 CFU/mL	10 000 000 CFU/mL
Others	500 CFU/mL	15 000 000 CFU/mL
Total Anaerobic Bacteria		
Sulfate Reducing	20 CFU/mL	10 000 CFU/mL
Clostridia	<10 CFU/mL	500 CFU/mL
Fungi		
Molds	5 CFU/mL	100 CFU/mL
Yeasts	<10 CFU/mL	6 000 CFU/mL
Microscopy		
Iron Bacteria	None detected	None detected
Sulfur Oxidizing Bacteria	None detected	None detected
Filamentous Bacteria	None detected	None detected
Algae - Filamentous	None detected	None detected
Algae – Non-Filamentous	None detected	None detected
Diatoms	None detected	None detected
Microscopy Other		
Organisms	None detected	None detected
Colorless Crystals	None detected	Very few

All counts expressed as Colony Forming Units per mL (CFU/mL) of sample

Figure 5.11 Illustration of the types of organisms typically found in water and deposit samples.

of a river water sample and a cooling tower basin deposit sample. The categories in the analyses are described briefly in the following paragraphs.

Bacteria

At the head of the list are aerobic bacteria. The total count is a measure of the variety of bacteria living together in a water sample. One of the most common is *Pseudomonas*, a slime-forming variety, which reproduces by fission. Others include spore-forming bacteria that can secrete a thick coating to encapsulate the cell and help it survive changes in temperature, food supply, and other shocks from the environment. Aerobic bacteria require oxygen and produce CO_2 as a by-product of energy production. These exist and survive only in oxygenated water. Some bacteria are facultative, meaning that they can live both in the presence and absence of dissolved oxygen. In lakes and rivers, oxygen content can vary by depth of the water, with the highest concentration at the surface.

The next major classification includes common anaerobic (oxygen-free environment) organisms. These bacteria use fermentation processes to breakdown food sources and produce energy. Some use sulfate in the water and produce sulfide that can cause corrosion in metal piping and equipment, especially beneath deposits where they are shielded from contact with dissolved oxygen. The bottom of deep lakes can be totally devoid of oxygen. Swamps, bogs, and some rivers may have low oxygen at the bottom of the water column, and deposits of decaying vegetation lead to fermentation of the organic matter. By-products of anaerobic bacteria are carbon dioxide, methane, hydrogen, ammonia, and hydrogen sulfide.

Other troublesome bacteria may be determined by microscopic observation of the water or deposit sample. These include iron-depositing bacteria, sulfur-oxidizing bacteria, and filamentous bacteria. When organisms other than those shown on the standard analytical form are found, these are noted in the appropriate location. For example, *Escherichia coli* is reported as aerobic, non–spore-forming bacteria.

Fungi and Algae

Fungi are molds and yeasts. They are important because of their ability to attack cooling tower lumber, deteriorate paper or textile products, and affect use of water in food production. Algae produce tastes and odors and interfere with flocculation and sedimentation processes for clarification of water. Like their larger plant relatives, they have certain blooming seasons during the year.

Identification of species of algae is done with the microscope. The analyst must be able to recognize the large varieties of blue-green and green algae and the delicately patterned diatoms that are part of this family of microorganisms.

Other Organisms

Organisms other than bacteria, fungi, and algae include protozoa and rotifers that are often found grazing on the floc containing other microorganisms. Protozoa are larger, single-celled organisms, and rotifers are multi-celled organisms. The presence of these species in a water sample generally indicates a higher level of biological contamination.

When wastewater is analyzed, it is generally necessary to determine fecal coliform and fecal streptococci to establish the need for final disinfection. Coliform bacteria and particularly fecal coliform are generally an indicator of the presence of pathogenic organisms that can be a health hazard. Effluent should be tested regularly and have coliform counts below a maximum value for a statistically significant number of samples to be considered safe for discharge.

If a bioassay is made of a stream to assess its health, a census must be made of many larger organisms. Macroorganisms, visible to the unaided eye, include a variety of worms, crustaceans, and larvae. A healthy stream contains a large number of species with relatively low populations. These provide food for higher forms of life, such as fish, crawfish, and shrimp.

Macrofouling

Surface water presents problems from growth of mollusks like clams or mussels in plant intake pipes and cooling system (Fig. 5.12). Macrofouling is the attachment of these complex organisms to piping and other surfaces of plant intake piping and cooling system. Macrofouling is most common in, plant intake pipes, once-through cooling systems or system water intakes using surface water, like lakes, rivers, or oceans. Shells of adult clams or mussels can plug heat exchanger tubes as shown in Fig. 5.13. Macrofouling costs are estimated to be in the billions of dollars on an annual basis for worldwide industries. This cost is related to plugged pipes and heat exchanger tubes, reduced water flow, under-deposit corrosion, damage to pumps, and the high cost of prevention or mechanical cleaning of macrofouling deposits.

Figure 5.12 A variety of Zebra mussels, which are typically about 5/8 inch (15 mm) in length. (*Courtesy of the United States Geological Survey.*)

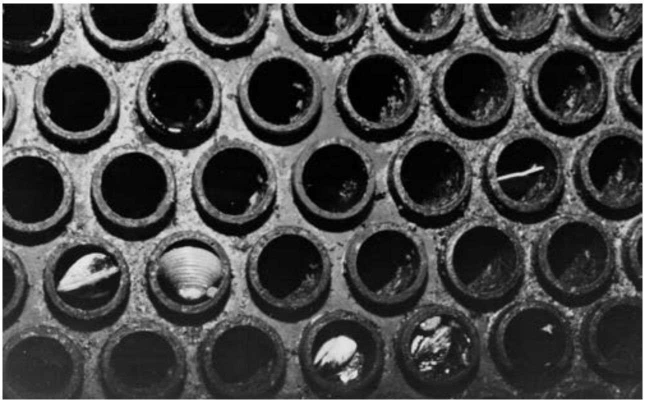

FIGURE 5.13 Small clams lodged in heat exchanger tube inlet end, preventing water flow through those tubes, reducing exchanger efficiency.

The various species of mollusks that cause macrofouling differ between freshwater, brackish, and seawater systems. Barnacles, bryozoa, oysters, and brown-, blue-, and green-lip mussels are examples of seawater and brackish water mollusks responsible for cooling water macrofouling. In fresh water systems, the most common species of concern are Asiatic clams, zebra mussels, gastropods, and bryozoa. Macrofouling can be caused by different species depending on location of the cooling system in the world. The species that receive the most attention as major problem sources are zebra mussels, Asiatic clams, and blue mussels.

Mollusks are invertebrates, characterized by a soft body, and most but not all have an outer shell. The Asiatic clam, blue mussel, and the zebra mussel are bivalves with a hinged, hard shell that covers a soft body. Two tubes channel water to and from a central cavity where there is a single pair of gills. Bivalves filter an average of 7.5 L of water per hour for respiration and feeding. Closure of the shell enables the bivalve to withstand adverse physical and chemical factors for a period. The organism can tolerate anaerobic conditions during the period that the shell is closed.

The life cycle of the blue mussel is shown in Fig. 5.14. This cycle is typical for most bivalves beginning with the larvae or veliger stage and continuing to the mature adult. A complete cycle occurs in about 6 to 9 months for most species, leading to rapid multiplication. When adult organisms in the water spawn, juvenile organisms called veligers are produced. The veligers are free-floating organisms and may be drawn into the water intake of a plant or a once-through system. The veligers can attach to system surfaces and grow into adult mollusks. When adults die, the shell may be released and plug tubes in heat exchangers.

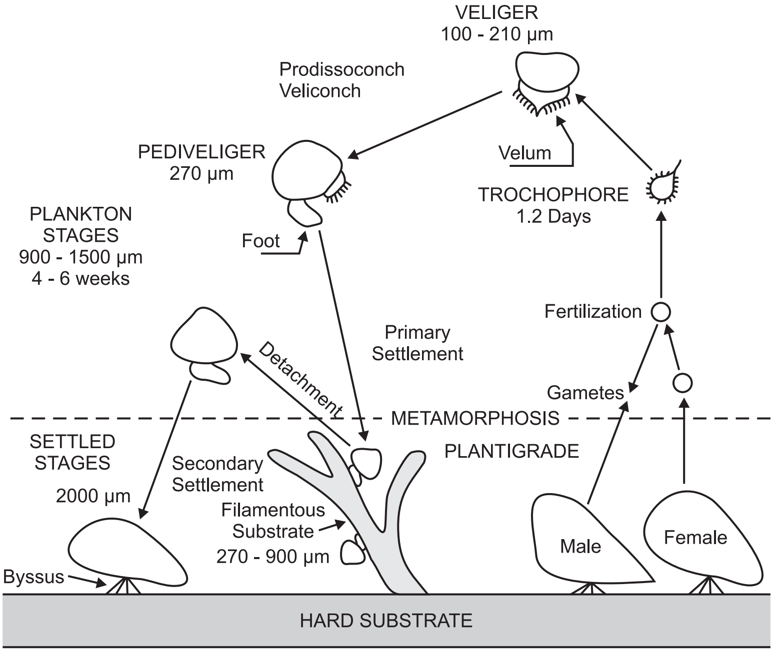

FIGURE 5.14 Life cycle of blue mussels.

The Asiatic clam was first observed in the United States in the 1930s having arrived from Asia. This species is also found in Mexico, Latin America, and Europe, and therefore, Asiatic clams are a global problem. The organisms multiply rapidly in waters with temperatures between 35 to 95°F (2–35°C). In the spring, the adults are able to release about 300 larvae on a daily basis. These mature within 6 to 9 months, and then as adults, are able to reproduce. The larvae and juveniles initially attach to surfaces and later tend to burrow into accumulated mud and silt in low-flow zones.

The zebra mussel is similar to the Asiatic clam in many respects. Zebra mussels reproduce when the adult releases mobile larvae into the environment. A mature adult may release as many as 40 000 larvae per year. The larvae are small and mobile and are able to pass through screens and settle on virtually any surface. Zebra mussels attach themselves to the surface through a sticky byssal thread. The ideal temperature for growth is lower than the Asiatic clam in that zebra mussels prefer water temperature of 68 to 77°F (20–25°C).

The blue mussel is an edible seawater organism and prefers to settle in low-flow environments in cooling systems. The shell of the adult is the main source of fouling problems.

Dissolved Gases

Dissolved gases like oxygen, carbon dioxide, nitrogen, oxides of nitrogen, and oxides of sulfur can significantly affect the quality of any water. For example, a deep well can contain anaerobic bacteria because oxygen has been depleted from the water. A healthy river or stream contains adequate amounts of dissolved oxygen to support a variety of species of fish. Biological activity can affect the balance of dissolved gases in water. For example, algae can cause an increase in the pH of a lake by consuming much of the dissolved carbon dioxide in the water. Several of these gases can affect the pH of groundwater or lake water.

The typical pH of almost all natural waters is 6 to 8, controlled mostly by the presence of bicarbonate alkalinity and some CO_2 dissolved in the water. All waters in contact with geologic formations, including limestone and dolomite minerals, tend to reach this equilibrium pH range as the result of chemical reactions that cause weathering of rocks, and oxidation-reduction reactions which are mediated by aquatic organisms. Because of this, the few exceptional streams that contain free mineral acidity (ie, have a pH below about 4.5) usually dissipate this condition by accelerated weathering of the alkaline components of the rocks they contact. Likewise, when the pH exceeds 8 and carbonate alkalinity begins to appear, this is brought into balance by reaction with carbon dioxide from the atmosphere or from respiration of aquatic life.

Uncontrolled discharge of industrial wastes can damage this natural buffering effect of the equilibrium between the aquatic environment, the atmosphere, and the lithosphere. In most parts of the world, legislation prohibits such discharge; therefore, the only circumstances that normally cause waters to fall outside the natural conditions are accidental spills of large volumes of strong chemicals, seepage of acid mine drainage into a stream, or acid rain from air pollution.

Acid rain is caused by the dissolution of acidic gases from the environment, chiefly the oxides of sulfur, like sulfur dioxide (SO_2) and sulfur trioxide (SO_3), and aggravated by nitrogen oxides (NO_x). The most prominent source appears to be emissions of sulfur from coal-fired power plants. When acid rain falls on alkaline rock or into rivers or lakes in limestone basins, there may be enough reserve alkalinity in the rock or dissolved in the water to neutralize the acidity. However, often rain falls in forested areas where vegetative litter has developed a soil high in humus. There is no natural alkalinity then to counteract acidity of the rainfall, and the runoff is acidic. If the drainage leads to a lake in a granite basin (or a formation free of limestone), the lake itself becomes acidic, and normal aquatic life disappears.

Water Reuse and Recycle

Whether it is called reuse, cascading, or recycle, the use of water that has already been used in another application brings added challenges along with potential savings in water and cost. Many factors must be evaluated when planning to reuse or recycle water in an institutional or industrial application. The first step is to determine the environmental and economic goals. Various water sources and the quality and variability of those sources must be evaluated to match the sources to water quantity and quality requirements of systems. Options for recycle should be optimized for both system performance and cost savings.

One of the major challenges is the use of low-quality water sources for recycle (Table 5.4). Often, water that has been discharged

Source	Ground Water	Surface Water	Municipal Wastewater	Refinery Wastewater	Sour Water Stripper Bottoms
Aluminum (Al)	<0.1	<2	0.1–0.5	<0.1	0.1–0.5
Iron (Fe)	<5	<2	0.1–1	0.1–2	0–10
Phosphate (PO_4)	<2	<3	6–12	1–10	0–3
Sulfate (SO_4)	10–100	5–50	100–200	100–2000	1–300
Chloride (Cl)	5–100	5–50	100–400	300–700	2–300
Nitrate (NO_3)	<2	<4	2–11	0–4	<3
Ammonia (NH_3)	<1	<1	5–25	0–20	5–70
Hydrogen sulfide (S)	0–2	<0.1	<0.1	<1	0–50
Phenols (C_6H_5OH)	<0.1	<0.1	<0.1	<0.1	200–400
Conductivity µS/cm	<1000	<500	1200–1600	2000–6000	200–1100
Suspended solids (Total at 105°C)	<2	1–25	<5	10–110	<2
COD(C)	<2	<5	20–80	20–280	430–4300
TOC(C)	<2	<10	10–20	10–130	65–1200

All values are in mg/L except conductivity, which is µS/cm.

Table 5.4 Comparison of General Ranges of Troublesome Contaminants in Three Wastewater Sources to Typical Concentrations Found in Reasonable Quality Ground and Surface Water Sources That May Be Used for Industrial or Domestic Uses from domestic or industrial applications contains higher contaminant concentrations or additional contaminants that increase the potential for the typical problems in water treatment applications:

- Corrosion due to increased chloride, sulfate, ammonia, or sulfide
- Scale due to increased calcium, magnesium, alkalinity, sulfate, phosphate, or silica
- Fouling from increased suspended solids, iron, manganese, aluminum, or organics
- Microbial growth from increased phosphate, ammonia, and organics

These problems can be made more severe by variability of the concentrations of various contaminants in the water stream to be reused. The result is that some type of pretreatment or intermediate treatment must be used to clean the water before it is reused or recycled. In other cases, additional treatment chemicals or methods may be required to minimize corrosion, scale, fouling, or microbial growth in the system that is using the recycled water. Pretreatment methods may be as simple as filtration or as extensive as membrane separation like reverse osmosis.

Finally, to achieve the desired goal, a strategy for reuse and recycle should be developed. The simplest options should be considered first, before progressing to successively more complex reuse and recycle methods. Water conservation should be one of the first options considered. Cascading water from one process in a plant to another, that has less critical water requirements, is the next option. This may be possible without intermediate treatment in some cases. Reuse of another wastewater source from outside the plant or recycle of a wastewater stream within the plant is generally the last consideration. These sources generally require some type of pretreatment before they can be used in industrial applications. Evaluating all the options gives the best opportunity to achieve the desired goal at the lowest cost.

SECTION 3.1

Applications—Impurity Removal

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CHAPTER 6

Raw Water Clarification and Filtration

The processes of coagulation and flocculation are employed to separate suspended solids from water, whenever natural subsidence rates are too slow to provide effective clarification. Water clarification, lime softening, sludge thickening, and dewatering depend on correct application of the theories of coagulation and flocculation for success. Depending on the water quality required, water treatment plants usually provide some degree of treatment, such as softening and water clarification. Water softening is the process of removing or reducing water hardness and possibly alkalinity. Water clarification is the process of removing suspended solids from water.

Taking surface water clarification as an example, raw water contains impurities in varying amounts. Before this water can be used for common industrial and household applications, it requires treatment to remove these impurities. Turbid water contains suspended matter with varying particulate sizes. Settleable solids are particles large enough to settle quiescently, while dispersed solids are particles that do not readily settle. A rule of thumb is that settleable solids are greater than about 10 µm, while dispersed solids are 1 to 10 µm. True colloidal solids are less than 1 µm.

A significant portion of non-settleable solids may be colloidal, and the colloidal and dispersed solids are the targets of coagulant addition. Each particle is stabilized by negative electrostatic charges on its surface, causing it to repel neighboring particles, analogous to magnetic poles repelling each other. Since this prevents particles from colliding to form larger agglomerates, termed *flocs*, the particles do not settle. Coagulation is the destabilization of these colloids by neutralizing the forces that keep them apart. This is generally accomplished by adding chemical coagulants with appropriate mixing

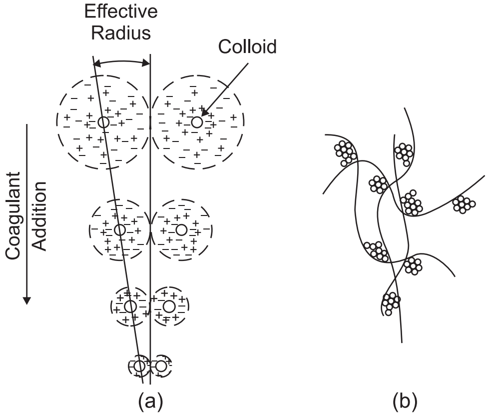


Figure 6.1 (a) Coagulation: Addition of a coagulant neutralizes charges, collapsing the "cloud" surrounding colloids, so that they can agglomerate. (b) Flocculation: Bridging by the flocculant chemical among agglomerated colloidal particles forms large, settleable flocs.

energy. Aluminum salts, iron salts, and polyelectrolytes are the chemicals usually used.

Figure 6.1 illustrates how these chemicals reduce the electric charges on colloidal surfaces, allowing the colloidal particles to collide and agglomerate into floc particles. These initially small flocs join, creating larger and larger agglomerates that become large enough to settle. The destabilization step is coagulation (charge neutralization); the floc-building stage is flocculation.

The terms coagulation and flocculation are often used interchangeably; however, when viewed as two different mechanisms, a better understanding of clarification and dewatering is provided. From a practical viewpoint, coagulants and flocculants are different, since flocculant polymers are very high molecular weight and require an inversion or dissolution step before being used to bridge particles. Coagulants are smaller molecules designed to neutralize the surface charge on the particle. Thus, they can be fed as a concentrated solution or diluted.

Water treatment plants provide efficient coagulation and flocculation of raw water by adding chemicals that provide a positive surface charge, as well as turbulent mixing of the chemically treated water.

Water filtration is the process of removing suspended solids from water during passage through porous granular materials. Sand filters are typical granular filtration units in both municipal and industrial water treatment plants, as a final polishing step before the water proceeds to the user. Granular filters can be single or multimedia and are available in three categories: gravity (several types), pressure, and upflow filters. Discussions of each filter category show the variety of designs available.

Coagulation

Water clarification depends on the application of the principles of coagulation and flocculation. At common water pH greater than the isoelectric point (>3), the surface of each particle in the water develops a negative electrostatic charge, repelling neighboring particles. Coagulation involves the neutralization of the electrostatic charge, enabling the particles to collide and form agglomerates.

These collisions, in turn, combine the particles into small groups, called flocs. The formation of flocs is called flocculation. Ideally, flocculation proceeds until the flocs become large enough to settle from suspension within a reasonable time (about 20 minutes).

Colloidal species encountered in raw water and wastewater include clay, silica, iron and other heavy metals, color, and organic solids. Colloids may also be produced in precipitation processes such as lime softening. Oil in wastewater is frequently colloidal.

Among the wide variety of colloidal materials in water, there is a broad distribution of particle sizes. Table 6.1 is based on Stokes' Law [Eq. (6.1)], which shows how particle size, density, and water viscosity relate to the settling rate.

$$V_o = \frac{G(\rho_1 - \rho_2)D^2}{18\mu} \tag{6.1}$$

where V_o = settling velocity, cm/s
G = gravitational force, cm/s^2
ρ_1 = particle density, g/cm^3
ρ_2 = liquid density, g/cm^3
D = particle diameter, cm
μ = liquid viscosity, dyne·s/cm^2

Typical Suspended Solid	Diameter (mm)	Diameter (μm)	Total Surface Area for Equal Mass	Settling Time to Fall 1 m
Gravel	10	10 000	314 mm^2	1 s
Coarse sand	1	1000	3140 mm^2	10 s
Fine sand	0.1	100	31 400 mm^2	125 s
Silt	0.01	10	0.314 m^2	108 min
Bacteria	0.001	1	3.14 m^2	180 h
Colloids	0.0001	0.1	31.4 m^2	755 d

Particles larger than 100 μm are visible to the naked eye and are considered settleable solids. In the range 10 to 100 μm, particles are considered turbidity. Below 10 μm, particles are considered colloidal. Particles larger than 0.1 μm are visible by light microscope; below 0.1 μm, the electron microscope is used for detection.

Table 6.1 Sedimentation of Small Particles of Silica (Specific Gravity = 2.65)

Equation (6.1) assumes hard, spherical particles. Note that the water viscosity affects settling (i.e., when the water is cold, the settling speed is slower). Table 6.1 shows that 10 µm particles settle in a reasonable period of 108 minutes. Colloids always require coagulation to achieve an effective size and settling rate; but even larger particles, which are not truly colloidal and would settle if given enough time, may require coagulation to form larger, faster settling floc.

When insufficient settling time is available in a treatment plant to remove suspended solids, coagulation and flocculation may cause them to grow in size and settle more rapidly to overcome the physical limitation of the plant design. In this case, the chemicals are being used as settling or sedimentation aids.

Colloids are categorized as hydrophobic (water hating) or hydrophilic (water loving). Hydrophobic colloids do not react with water; most natural clays are hydrophobic. Hydrophilic colloids react with water; organics causing color are hydrophilic. Of importance in water treatment, hydrophilic colloids may chemically react with coagulants used in the treatment process. Therefore, hydrophilic colloids require more coagulant than hydrophobic colloids, which do not chemically react with coagulants.

Several theories have been advanced to describe the colloidal particle and the forces surrounding it. For practical purposes, the determination of the nature and strength of the particle charge is all that is needed to define the colloidal system. The particle charge strength, illustrated as the layer surrounding the colloid in Fig. 6.1, affects how closely colloids can approach each other.

Contaminants Removed

Suspended solids and color are the two major impurities removed during clarification. Through various clarification techniques, iron, manganese, and silica may also be partially removed, but total dissolved solids (TDS) are not reduced. TDS may actually increase when using clarification aids containing aluminum or iron salts. Organic materials contributing to taste and odor problems may be reduced through proper chemical treatment.

Water quality objectives of municipal and industrial water treatment plants vary greatly, depending on the quality of the incoming water, the intended uses for the finished water, and the economics of the treatment processes used. The following sections discuss major impurities in water in terms of problems each impurity can cause, and the importance municipal and industrial plants place on its removal.

Suspended Solids (Turbidity)

Many water supplies are turbid, containing suspended matter varying in concentration from a trace in deep wells to thousands of mg/L in some rivers. Suspended solids include such materials as fine sand, silt, clay, decomposed vegetation, bacteria, algae, and other microbiological organisms.

The amount of these impurities varies significantly in some water sources. In a river after rain, suspended solids due to sand, silt, and clay may increase rapidly. During rainy periods, such as in the spring, rivers may run very turbid for several weeks, only to be extremely low in turbidity during the driest days of summer. Algae and other microorganisms may be present at certain times of the year, making treatment more difficult, and at other times may be so low that they have no effect on clarification.

The most common measure of the amount of suspended solids in water is turbidity, which is a measure of the clarity of the water and may be obtained in several ways.

The preferred turbidity unit is the nephelometric turbidity unit (NTU). Drinking water must contain less than 0.5 NTU, as required by state and federal government standards, although some plants have requirements that are more stringent. Most surface water sources are less than 100 NTU, though a muddy river may rise as high as 4000 NTU for brief periods.

Note that the Jackson turbidity unit (JTU) is an obsolete turbidity method that measures when a candle can no longer be seen through a standardized cell and clay suspension. In general, there is no correlation between JTU and NTU, although site-specific correlations are possible.

The most widely used turbidity measurement technique is the nephelometric or light scattering method. A nephelometer employs an incandescent light source directed into a water sample. The suspended particles scatter light as the beam passes through the sample, with the intensity of the scattered light being related to the number, size, and color of the particles. A photodetector is placed at right angles to the light beam and detects the intensity of light scattered.

Another method is the Helige Comparator. The operator makes a turbidity measurement based on a visual comparison. As with all visual comparator methods, the results are extremely operator dependent. In addition, the unit is not as sensitive as the nephelometer, especially at low turbidity readings; consequently, the comparator is no longer commonly used.

Some spectrophotometers have a turbidity measurement using the formazin turbidity unit (FTU). This measurement is different from NTU, as the instrument detects how much light passes through the water sample. Light that did not reach the detector is assumed to be scattered light. This method is acceptable, and the correlation between NTU and FTU is linear. Either instrument can be used to measure turbidity, as long as the units are reported. The exception is in waters that are highly colored, where absorbed light is assumed scattered light, and FTU results tend to be higher than NTU results for the same sample. In addition, since FTU measures lost photons, it measures a larger number of lost photons versus NTU, which detects scattered photons at a 90° angle from the light source.

Municipal water systems produce potable water, and in the United States, they are affected by the guidelines of the Safe Drinking Water Act. All around the world, water plants must meet certain water quality requirements to assure the production of safe, healthful water. One line of defense against bacteria and other detrimental materials entering the water system is good coagulation in the water plant. The clarity of water is the easiest measure of complete coagulation. In the United States, the law varies with region, but a rule of thumb is a turbidity limitation of 0.5 NTU for finished water. Many plants produce water less than 0.5 NTU and use their historical turbidity level as the standard for good water. Note that these turbidities are measured immediately after the filter (in the clearwell). Home tap water turbidities can be higher due to distribution system contamination, disinfection, etc.

Many industrial plants making non-potable water often require 1 NTU quality. Generally, a plant wants to produce less than 5 NTU water from the sedimentation basin. This water can be acceptable for various processes, depending on the specific process requirements. However, excessive turbidity may cause fouling of heat transfer surfaces and reduce efficiency of some systems. If filtration is utilized, finished turbidity of less than 1 NTU is often obtained. In some cases, low turbidity is imperative to good plant operation, such as in boiler pretreatment where ion exchange or reverse osmosis (RO) precedes boiler makeup, following clarification or cold lime softening. Turbidity can foul ion exchange media, leading to channeling through the media bed. In RO systems, high turbidity causes a high silt density index (SDI), which leads to colloidal fouling of RO membranes. Excessive fouling could lead to expensive increased cleanings, or in the worst-case scenario, could lead to very expensive membrane replacement. Low turbidity water does not guarantee low SDI for the RO water influent, because particles smaller than 1 μm do not scatter light and are thus, not detected using turbidity measurements.

Another means of measuring suspended solids is particle counting. Particle counters are increasingly popular due to reduced costs and improved reliability (especially with the commercial development of diode lasers and low-cost computing). In addition, particle counters are more sensitive to changes in finished water quality compared to turbidity. For example, it is common to monitor sand filters for turbidity breakthrough as a measure of effluent quality, since many filtrate specifications involve turbidity, it is often used to trigger a filter backwash. Particle counters are more sensitive than turbidimeters and can be an early warning for systemic filter issues. Generally, particle counts start to increase before turbidity increases, indicating the filter capacity has been reached and a backwash should be initiated.

Particle counters generally measure individual particles; therefore, they are limited to relatively clean (<1 NTU) water. They are also different from particle sizers. Because particle sizers can handle higher solids (even slurries), sizers measure particle size via indirect methods. True particle counters measure individual particles.

There are two types of particle counters: light scattering and light extinguishing. Light scattering is similar to nephelometric turbidity, except the excitation wavelength is well defined and the scattered light is measured as a function of the observation wavelengths. From the scattered light intensity as a function of wavelength, the particle size distribution is determined using complex equations that are beyond the scope of this book. Light scattering is extremely sensitive, being able to measure sub-micron size particles. Due to the data processing and sensitivity, these particle counters are suitable for clean water applications.

Light extinguishing particle counters function, by blocking light as a single particle passes through a light beam, which is usually a laser beam. The larger the particle, the more light is blocked. This reduction in light is calibrated to a particle size. While the particle may be irregular, the counter reports the particle as an average circular cross-section spherical equivalent. Because individual particles are counted, these instruments are limited to approximately 20 000 particles/mL. In addition, for optical and electronic reasons, light extinguishing particle counters can measure down to approximately 2 μm in diameter.

Color

Surface water runoff carries organic material leached from vegetation into streams and lakes, adding color to the water. Color is usually associated with naturally occurring tannins and lignins and is measured by a visual comparator procedure against platinum cobalt color standards or using color meters. These standards are solutions prepared from platinum and cobalt salts and are the bases for the American Public Health Association (APHA) color scale. Color is reported in APHA color units.

The majority of industrial plants do not put a specification on color in the finished water. For plants with highly colored water sources (>30 APHA), a color specification of 10 APHA is often established, especially if the water is going to demineralizers or used in making white paper.

Zeta Potential

Zeta potential is a measurement of the electrostatic charge on a particle. For colloids in natural water sources in a pH range of 5 to 8, the zeta potential is generally −14 to −30 mV; the more negative the number, the stronger the particle charge. As the zeta potential approaches zero, particles can approach one another more closely, increasing the likelihood of collision.

In a conventional clarification system at pH 6 to 8, coagulants provide positive charges to reduce the negative zeta potential. Coagulation usually occurs at a zeta potential that is still slightly negative;

complete charge neutralization is not required. The optimal zeta potential required for coagulation varies, depending on the chemical coagulant mechanism and the measurement technique used. If too much coagulant is added, the particle surface becomes positively charged (a positive zeta potential), and the particles are redispersed; this is called charge reversal.

Coagulants may be required in high pH water treatment systems, such as in lime softening. Calcium carbonate ($CaCO_3$) particles carry a negative charge, and cationic coagulants are useful in reducing residual colloidal hardness, presumably by agglomerating colloidal $CaCO_3$. Magnesium hydroxide [$Mg(OH)_2$], on the other hand, carries a positive charge until the pH exceeds 11. In lime or lime-soda softening processes, where both $CaCO_3$ and $Mg(OH)_2$ precipitate, the oppositely charged particles coprecipitate. This coprecipitation in past geologic periods produced the mineral dolomite ($CaCO_3 \cdot MgCO_3$). In waters that are severely acidic ($pH < 3$), the natural particulate charge could be cationic, and then anionic coagulants would be needed for charge neutralization.

Zeta potential is determined indirectly from data obtained in observing particle motion under a microscope. Zeta potential measurements have been used successfully to monitor plant coagulant dosages. However, for selecting the best coagulant, zeta potential readings alone are not reliable. Observation of results in a jar test remains the best method of coagulant selection.

Somewhat related to zeta potential in a qualitative way is streaming current, an electric current produced when colloidal particles are trapped in a capillary tube or confined space with water flowing past them at high velocity. The adsorbed charges, or counter-ions, are stripped from the surface of the colloid and pass along with the water, until the velocity is dissipated. The flow of ions constitutes an electric current that is measurable by an instrument called a streaming current detector (SCD). As is true with zeta potential, if coagulants have neutralized the charge on the colloids, the current is reduced. Note that an SCD is only sensitive to particles that transiently adsorb to the piston's wall. Particles that do not adsorb are not detected. This may partially explain why optimal coagulation usually occurs at a slightly negative surface charge, because particles are neutralized but not detected.

Streaming current detectors require frequent maintenance to control plugging of the close clearances in the water passages and are sensitive to pH swings. In many cases, the head of the detector (a piston or plunger reciprocating in a closed cup) can be kept clear by an ultrasonic cleaning device. SCD can produce an output signal to control the coagulation process. One of the variables that need study in each system is the time factor; the speed or rate of charge neutralization varies with the type of colloid present and with temperature. Therefore, a sample taken immediately after coagulant addition is usually inadequate. Typically, an equilibration time of 5 to 10 minutes is needed before putting the sample through the SCD.

Mixing is required to supplement coagulant addition to destroy stability in the colloidal system. For particles to agglomerate, they must collide, and mixing promotes collision. Brownian movement, the random motion imparted to small particles through bombardment by individual water molecules, is always present as a natural mixing force. However, additional mixing energy is usually required. High-intensity mixing, which distributes the coagulant and promotes rapid collisions, is most effective. The frequency and number of particle collisions are important in coagulation. In low-turbidity water, the addition of solids such as clay, or the recycle of previously settled solids, may be required to increase the number of particle collisions.

Flocculation

The floc formed by the agglomeration of several colloids may not be large enough to settle or dewater at the desired rate. This is termed pin floc because of its small size. In such situations, a flocculant gathers together floc particles into a net, bridging from one small agglomerate to another and binding the individuals into large agglomerates as shown in Figs. 6.2 and 6.3. The increase in size also increases the probability that small, unreacted primary particles can adsorb onto

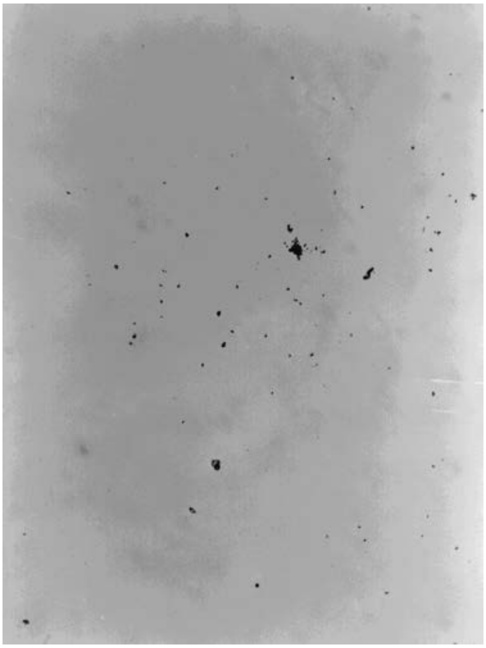


Figure 6.2 Turbid river water photomicrograph showing fine dispersion of tiny particles.

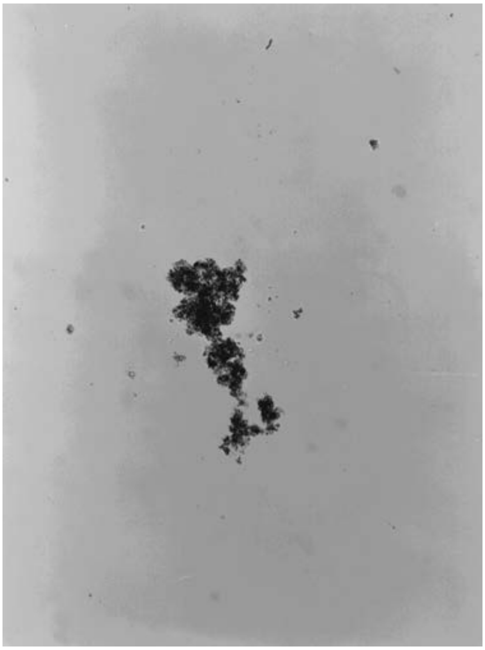


FIGURE 6.3 The same water treated with coagulant. Particles are collected in the floc (130×).

the large, net-like agglomerate surface. High molecular weight polymers are common flocculants. Flocculation is promoted by slow mixing, which brings the flocs gently together. Excessive mixing velocity shears the floc, and they seldom reform to their optimum size and strength without additional polymer treatment. Flocculation not only increases the size of floc particles, but it also affects the physical nature of the floc. Sludges and slurries, when flocculated, dewater at faster rates on sand beds and in mechanical dewatering equipment, because of the less gelatinous structure of the floc.

It is apparent that the processes of charge neutralization, or coagulation, and floc building, or flocculation, are so different that each system containing the chemically treated solids being processed has its own physical constraints. These are outlined in Table 6.2.

In an attempt to develop a mathematical procedure to express some of these variables, hydraulic engineers developed the concepts of velocity gradient and shear rate, or *G* factor. Figure 6.4 illustrates the basis of these concepts. In this illustration, the differential velocity between two particles 0.01 ft (3 mm) apart is 0.25 ft/s (76 mm/s), and the shear rate is 25/s. Obviously, it is impractical to measure the *G* factor in this way, but fortunately, further development of the mathematical model shows that shear rate is also related to the rate of energy input (power) per unit volume (equivalent to detention time

Variable	Coagulation	Flocculation
Nature of solids	Numerous, fine particulates	Scattered, large gels
Type of chemical applied	Low molecular weight charge neutralizer	High molecular weight particle binder
Energy requirement	Rapid mixing	Slow stirring
Velocity gradient	High	Low
Time in process	Seconds	Minutes

Table 6.2 Constraints between Coagulation and Flocculation

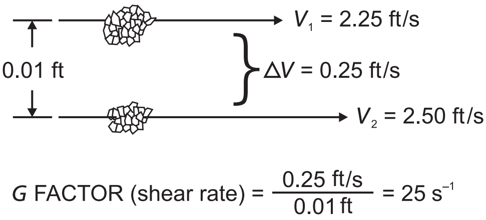


Figure 6.4 Illustration of velocity gradient and shear rate.

in the process) and water viscosity. The latter has a direct bearing on the frequency of particle collisions and explains, in part, the strong influence of water temperature on both coagulation and flocculation. Equation (6.2) shows the formula for *G* factor:

$$G \text{ factor} = \left(\frac{P}{[V \cdot \mu]}\right)^{0.5} \tag{6.2}$$

where G factor = velocity gradient, s^{-1}
P = power input, ft · lb/s (W)
V = volume, ft^3 (m^3)
μ = viscosity, lb · s/ft^2 (Pa · s)

The *G* factor usually recommended for most coagulation units is about 900/s for a 30-s mixing time, varying inversely with time. The required mixing time is usually established by bench tests, as described later. The recommended *G* factor for flocculation is lower, varying from about 50/s for cold, colored water carrying a very fragile floc to about 200/s for a solids contact lime softener on warm river water. Again, the *G* factor for flocculation must be determined by bench testing, and this should lead to a flocculator design that can be varied in speed and power input, as water conditions change, leading to fluctuations in solids concentration and sensitivity of floc to shear.

Coagulation and Flocculation Chemicals

Historically, metal coagulants (aluminum and iron salts) have been most widely used in water clarification. These products function primarily as coagulants. When added to water, they form positively charged species in the typical pH range for clarification (about 6–7). The hydrolysis reaction produces insoluble gelatinous aluminum or ferric hydroxide:

$$Al_2(SO_4)_3 + 6H_2O \rightarrow 2Al(OH)_3 + 3H_2SO_4 \tag{6.3}$$

$$FeCl_3 + 3H_2O \rightarrow Fe(OH)_3 + 3HCl \tag{6.4}$$

Note that the by-products are hydroxide precipitates and mineral acids, which react with alkalinity to reduce system pH and produce carbon dioxide (CO_2) as a secondary by-product. Sometimes, the gaseous CO_2 by-product interferes with the coagulation process by forming small bubbles, which adsorb onto the hydrous precipitate and cause floc flotation rather than settling. Dissolved gasses can also be an issue when water is warming, as water releases some of its dissolved gas during the settling portion of clarification, which can take hours.

Even if there are no suspended solids in the water initially, metal coagulants form floc, which enmesh destabilized colloids. However, the voluminous sludges produced by addition of metal coagulants create disposal problems, because they are usually difficult to dewater. This is why aluminum and iron salts are not often used to improve efficiency of centrifuges, filter presses, and other dewatering devices.

Metal coagulants are particularly sensitive to pH and alkalinity. If pH is not in the proper range, clarification is poor, and iron or aluminum may be solubilized and cause problems to the water user. The lower the coagulant dosage, the more sensitive the floc is to pH changes (Fig. 6.5). Table 6.3 lists some important properties of common coagulants.

The introduction of activated silica in the 1940s significantly improved performance of aluminum and iron salts in water clarification. The subsequent development of a variety of organic polymers called polyelectrolytes in the 1950s was an even more spectacular contribution to water treatment technology.

Polyelectrolytes are large water-soluble organic molecules, made up of small building blocks called monomers, repeated in a long chain. They usually incorporate ion exchange sites, which give the molecule an ionic charge. Those having a positive charge are cationic, and those with a negative charge are anionic. These molecules react with colloidal material in the water by neutralizing charge, or by bridging (tying together) individual particles to form a visible, insoluble precipitate or floc.

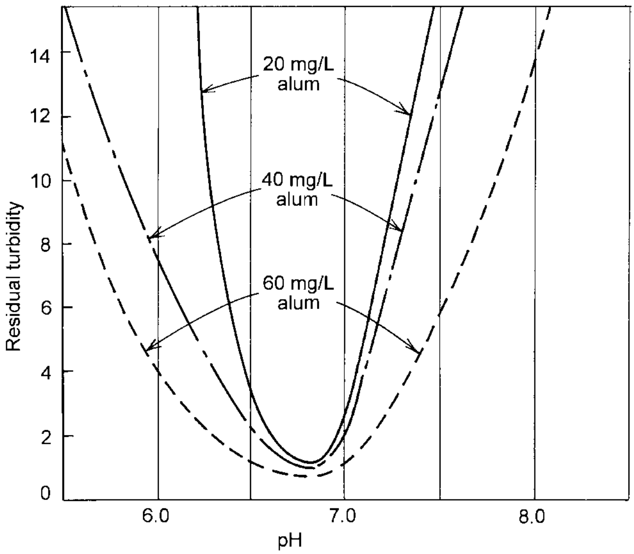


Figure 6.5 Effect of coagulant dosage on pH range limitations. The optimum pH remains almost constant, but the pH range becomes less restrictive as the coagulant dosage increases.

Common Name	Formula	Formula Weight	Equivalent Weight	pH of 1% Solution
Alum	$Al_2(SO_4)_3 \cdot 18H_2O$	666	111	3–4
Ferric chloride	$FeCl_3 \cdot 6H_2O$	270	90	3–4
Ferric sulfate	$Fe_2(SO_4)_3 \cdot 3H_2O$	454	75.7	3–4
Ferrous sulfate	$FeSO_4 \cdot 7H_2O$	278	139	3–4
Sodium aluminate	$Na_2Al_2O_4$	164	27.3	11–12

Table 6.3 Properties of Common Inorganic Coagulants

Polyaluminum chloride (PACl) is a generic term for a range of products that were initially developed in Japan in the 1970s. PACl minimizes the alkalinity consumption problem, because these materials incorporate some of the required alkalinity to form aluminum hydroxide. These products are essentially partially neutralized aluminum chloride and have the empirical formula $Al(OH)_xCl_{(3-x)}$.

From the empirical formula, aluminum hydroxide would have "*x*" equal to 3 with the aluminum +3 valence completely neutralized by hydroxide. Zero hydroxide is simply aluminum chloride ($AlCl_3$).

Aluminum hydroxide (three hydroxides and zero chlorides) has a basicity of 100% with basicity defined as:

$$\text{Basicity} = \frac{x}{3}(100) \tag{6.5}$$

where x = moles of OH^- and moles of $Al^{+3} = 1$.

The basicity of a given PACl product is an averaged parameter with the actual aluminum speciation being a complex mixture that can vary from monomeric aluminum (Al^{+3}) to a range of partially neutralized PACl molecules. Precise aluminum distribution is complex and the subject of much debate that is beyond the scope of this book.

Tailoring Polyelectrolytes

The performance of these materials can be modified to suit the nature of the colloidal matter to be removed from water. These modifications include variations in molecular weight and ion exchange capacity. These materials can also be produced without an ionic charge; these are called nonionic polymers. Although they are not, strictly speaking, polyelectrolytes, nonionic polymers exhibit many of the same flocculating properties in solution, and are considered as part of the general polyelectrolyte family of compounds.

Although most polyelectrolytes are synthetic organic materials, nature produces an endless variety of such materials. Some of these are chemically processed to improve performance and are commercially available. The cationic polyelectrolytes are either polyamines or quaternary amines. In water, a polyamine hydrolyzes as follows:

$$RNH_2 + HOH \Leftrightarrow RNH_2H^+ + OH^- \tag{6.6}$$

Because the hydrolysis yields hydroxide (OH^-), at high pH, the equilibrium reaction is forced to the left, and the polymer becomes nonionic. This is illustrated by Fig. 6.6, which shows loss in exchange capacity for a specific polyamine as pH increases. In contrast, the quaternary polymers are but slightly affected by pH, remaining positively charged over a broad pH range.

Anionic polymers incorporate a carboxyl group (COOH) in their structure. These ionize in the following manner:

$$RCOOH \Leftrightarrow RCOO^- + H^+ \tag{6.7}$$

The hydrogen ion forces the equilibrium reaction to the left, and anionic polymers become nonionic at low pH.

The ionic nature of polyelectrolytes is only one factor determining the performance of these materials as coagulants and flocculants. Other factors, such as the polar nature of nonionic bonds in the molecule, molecular size, and molecular geometry, play a large part, and may in some cases, overshadow the effects of charge and charge density. Hence,

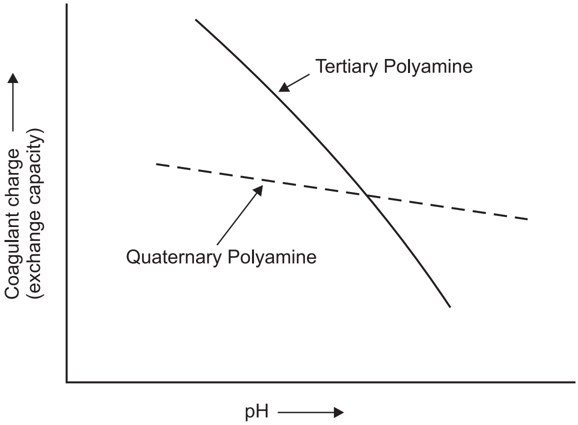


Figure 6.6 Generalized plot showing loss of cationic strength for tertiary polyamines as pH increases and relative pH independence of quaternary amine coagulants.

high molecular weight nonionic polymers are effective flocculants in many systems, because of their ability to attract and hold colloidal particles at polar sites on the molecule. Furthermore, because of their molecular size, they can bridge together many small particles. Less sludge is generated by organic polymers than by inorganic salts, since they do not add weight or chemically combine with other ions in the water to form a precipitate. Organic polymers do not affect the pH of the water and generally do not require pH adjustment for effective use.

As a rule, cationics are designed to work at lower pH values, anionics at higher. Nonionics and quaternaries are only slightly influenced by pH. The general rule should not be interpreted to mean that anionic polymers do not work at low pH; it simply means they are no longer ionic. They may produce good results in flocculating solids at low pH simply because of their nonionic bonds. The same applies to cationics; even though they are not charged at high pH, they may act as effective coagulants because of their polar groups.

Organic polymers overcome many of the problems inherent in the use of aluminum or iron salts. Depending on the selection of monomers and processing methods, a wide variety of polymers can be made of various configurations and molecular weights. Molecular weight is proportional to polymer chain length; the wide selection of structures and molecular weights makes it possible to design a polymer specifically for a given coagulation or flocculation problem, but this is seldom practical for economic reasons.

Organic polymers used in water treatment are of two major types, coagulants and flocculants. Coagulants are positively charged molecules of relatively low molecular weight. Although they exhibit some tendency for bridging, they are not particularly effective flocculants.

Flocculant polymers have much higher molecular weight, providing long bridges between small flocs to enhance particle growth. Flocculants are cationic, anionic, or nonionic. The flocculant that works best in any system can be determined only through laboratory screening and in-plant testing. Polymer flocculants, unlike coagulants, are not selected for neutralization, but rather for the ability to bridge and entangle pin floc.

Unlike inorganic salts, polymers do not produce voluminous, gelatinous floc. In applications where additional solids improve results, inorganic coagulants or clay may be required to supplement polymers. Polymers do not affect pH, nor is their performance as sensitive to the pH of the treated water as metal coagulants.

Activated Silica

Some inorganic compounds can be polymerized in water to form inorganic polymer flocculants. Activated silica (sometimes identified as SiO_2) is an example. When sodium silicate, which contains alkali, is diluted to 1.5 to 2.0% and then partially neutralized (usually with chlorine or sodium bicarbonate), the silica becomes colloidal and then begins to slowly polymerize. After aging for 15 to 30 minutes, the solution is diluted to about 0.5 to 1.0% SiO_2, arresting further polymerization and producing activated silica. Although this preparation procedure is complicated, this is a very effective flocculant for such applications as assisting alum treatment for color removal, and improving the softening of organic-containing waters.

Coagulation and Flocculation Applications

A sample of turbid water in a graduated cone separates into two layers, the settleable and the colloidal solids (Fig. 6.7). In raw water clarification, a coagulant is usually used, since the colloidal haze must be removed to produce the low turbidity demanded by most water-using processes. In wastewater clarification, a coagulant is required only where the suspended solids create a problem in meeting effluent guidelines; here a flocculant may be required to speed the settling rate.

Two types of laboratory tests are used to select the best chemical and approximate dosage level required for clarification: jar test and cylinder test. The jar test is used when the stream to be clarified has less than approximately 5000 mg/L suspended solids. Raw water clarification, settling of biological solids, and most primary waste streams are in this category. The cylinder test is used for heavy slurry streams where suspended solids exceed approximately 5000 mg/L. Coal and mineral processing wastes and the sludge resulting from a primary clarification are examples of heavy slurries.

The jar test simulates the types of mixing and settling conditions found in a clarification plant. The laboratory unit for running these tests (Fig. 6.8) allows up to six individual tests to be run simultaneously.

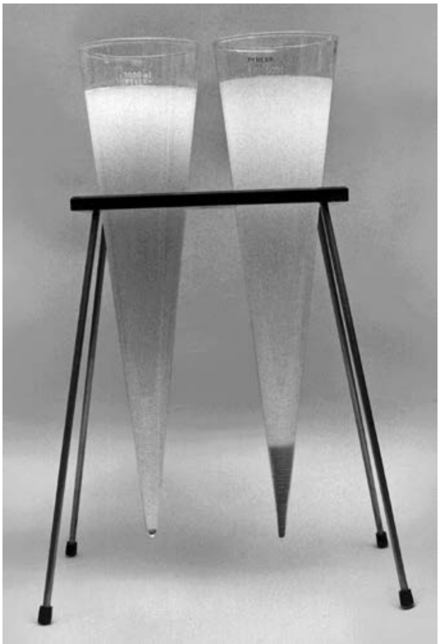


Figure 6.7 Solid particles in the left cone are a conglomeration of materials of various particle sizes, identified as suspended solids. After settling for 30 minutes, two fractions are obtained (right cone), settleable solids and turbidity.

Figure 6.8 This type of gang stirrer is widely used for jar testing, as both a research tool and a plant control device.

The jar tester has a variable speed motor allowing control of the mixing energy in the jars. A basic jar testing procedure would have a brief fast mix (about one minute) to properly disperse treatment chemicals. Then a slow mix time, about ten times longer than the fast mix duration, is used to promote agglomerates. Finally, a settling period at least as long as the slow mix is performed to simulate settling. The purpose of jar testing is to simulate plant performance and the combination of fast/slow/settling times is adjusted to approximately match the full-scale system performance.

Clarification results are sensitive to chemical dosage, mixing energy, and length of mixing. Figures 6.9 to 6.12 show a typical sequence in jar testing where a colloidal haze is removed. The coagulant is added with high energy to disperse it in the water and promote an increased frequency of collisions. The duration may be short, less than one minute. The actual mixing time is refined as the test regimen proceeds, in essence defining the optimum *G* factor. A polymer flocculant, if required, is added during the last few seconds of the rapid mix. In the slow-mix period that follows, floc-building proceeds until the floc becomes so big that shear forces finally overcome the bridging forces, breaking the floc apart. This limits the size

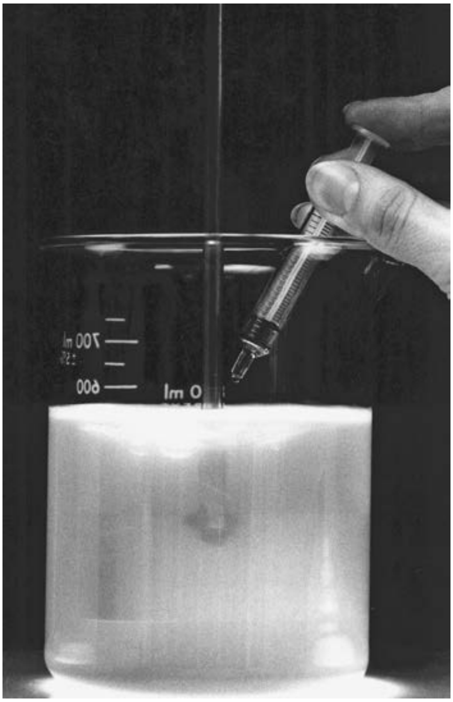


Figure 6.9 Coagulant is measured into a sample of turbid water with a high degree of mixing.

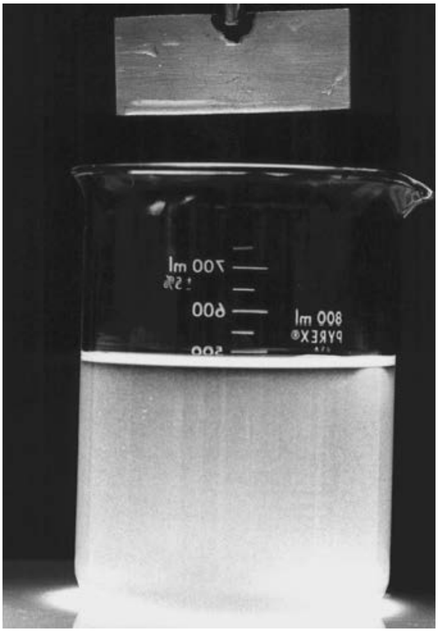


Figure 6.10 After coagulant addition, particle growth occurs because of charge neutralization. Additional coagulant or a high molecular weight flocculant may then be added.

Figure 6.11 After flocculation at a very low stirring speed (typically 10–15 rpm), the sample is examined after an established time. Note the fine pin floc, which has escaped entrapment by the larger floc.

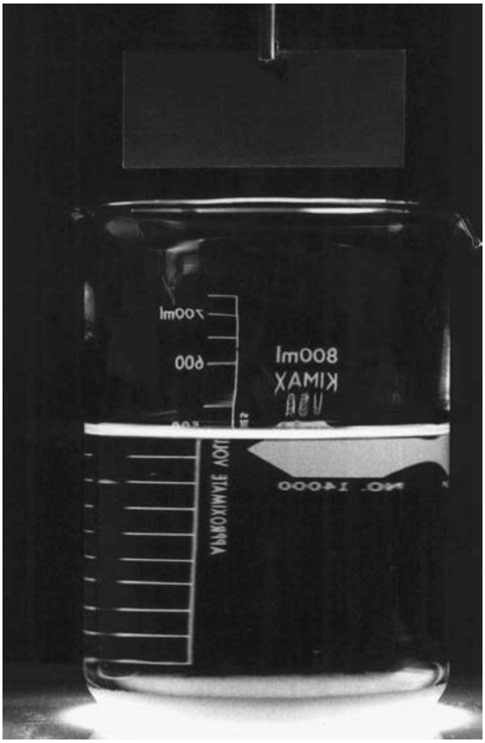


Figure 6.12 The supernatant is examined and tested after 5 to 10 minutes settling time, and the nature and volume of the floc is recorded.

of the floc. After slow mixing for an optimum period, found only by repeated tests (usually 5–20 minutes), the jars are allowed to settle for 5 to 10 minutes.

Jars with different chemicals, or the same chemical at different dosages, are run side-by-side and the results compared. Floc settling rate, final clarity or suspended solids, and volume of sludge produced (if measurable) are contrasted among jars. Although the eye can judge clarity, the more accurate standard measurement is made with a turbidimeter. Other quality tests such as pH, biochemical oxygen demand (BOD), color, chemical oxygen demand (COD), particle counting, and soluble metals, can be run on the settled water to establish performance standards.

A dosage series should always be performed to ensure accurate, relative test results. Figure 6.13 shows a generic dosage profile using a coagulant such as alum, which is represented by the dashed line. At a critical concentration, the water quality response (such as turbidity) quickly changes, and levels out with increasing dosage. In this situation, adding more alum does not improve performance, it only wastes chemical and increases treatment costs.

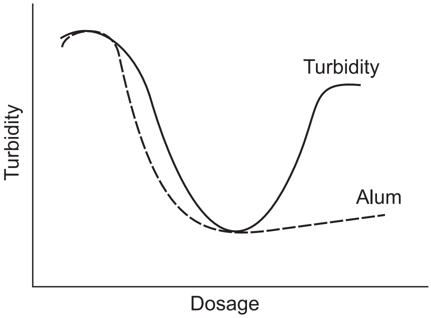


Figure 6.13 Typical jar test dosage profile.

The same figure shows the dosage profile for a polymeric coagulant (solid line), and it illustrates distinctly different behavior. Here, there is the same critical concentration, but with increasing dosage, the finished water quality degrades due to redispersion of the solids. With some treatment chemistries, there is a potential false minimum at a higher dose; therefore, a dosage profile is critical for proper coagulant selection.

The cylinder test, designed to indicate how fast the suspended solids settle, employs a 1000-mL graduated cylinder, stopwatch, and lab ware for dosing the chemical being evaluated. The slurry sample is placed in the cylinder, chemical is added, and the cylinder gently inverted several times. Mixing is much less severe than in the jar test, because solids are present at much higher levels and frequent collisions can occur at the lower mixing energy. After mixing, the cylinder is set upright, and the interface between the water and the settling solids observed. Time and solids level are recorded, and the data are plotted on a graph. As in the jar test, a number of analytical tests can be run on the clear water; however, rapid settling rate is usually the goal. By running coagulants and flocculants at different dosages and comparing settling rates, the most effective products are selected. Figure 6.14 illustrates the results of cylinder tests.

Color Removal

The selection of an effective chemical program for the removal of color from water, is accomplished by jar testing. The floc produced from coagulated organic matter is fragile, and the jar test device must be operated in a manner that duplicates mixing energy and flocculation shear corresponding to full-scale equipment.

For the most part, color in water is a mixture of colloidal organic compounds that represent breakdown products of high molecular weight substances produced by living cells. These materials are analogous to the polyelectrolytes used in water treatment. In fact,

Figure 6.14 Cylinder test showing the stages of mixing and settling.

natural organics like starch have been used as both dispersants and flocculants since the earliest days of water treatment. Natural organics are variously identified as humic acid (a polymer containing phenolic groups), polysaccharides (polymers similar to sugar and cellulose), polypeptides (protein polymers), and lignins and tannins (relatives of cellulose). For the most part, these substances are anionic or nonionic polymers. It is not surprising that cationic materials coagulate them, and the amount of coagulant needed tends to be proportional to the color.

Alum is commonly selected as the first coagulant to be evaluated in the jar test. After the alum demand has been satisfied, excess alum produces a floc that ties the coagulated particles together. The pH range is extremely narrow, usually about 5.0 to 5.8, and variation in pH usually disperses the floc and creates a haze. Most natural colored waters are low in alkalinity, and the alum used for coagulation often destroys the natural alkalinity. The addition of an alkali may be needed for pH adjustment. After coagulation and formation of the alum floc, an anionic polymer is usually used to strengthen the floc and aid sedimentation. A complicating factor is temperature; many colored waters are found in Canada, the northern United States, and Northern Europe where the selected program must be effective at 32°F (0°C), where viscosity greatly increases shear forces, and hinders sedimentation, complicating the jar test procedure. Another potential complication is the usual need for pH correction of the finished water to render it less corrosive than water at pH 5.5. The color matter in water behaves much like an acid-base indicator, and an increase in pH usually results in a color increase.

Certain cationic polyelectrolytes are useful for partial replacement of alum in the color removal process, permitting treatment at higher pH and reducing alkalinity destruction by the high alum dosage otherwise required. Table 6.4 compares the results of a conventional alum program to alum-polyamine treatment.

	Conventional Alum Program	Alum-Polyamine Program
Alum dosage, mg/L	55	35
Aluminate dosage, mg/L	40	30
Nonionic polymer, mg/L	0.5	None
Polyamine, mg/L	None	5
Final pH	5.2	6.5
Final color	5–10	5–10

Florida swamp drainage at 400 APHA color.

Table 6.4 Chemical Treatment of Colored Water

PACl can be used in partial alum replacement strategies, which are based on treatment costs in addition to performance. This is especially important in situations where significant finished water pH adjustment is required. Here, the cost of pH adjustment can be significant, especially if the safety aspects of handling large amounts of corrosive chemicals are considered. In addition, sludge disposal costs can be significantly reduced by reducing alum usage. Sludge is a factor to be considered during discussion of water treatment, because the amount and type of sludge are direct results of water treatment processes. Sludge disposal can be a major economic factor associated with the total cost of operation (TCO).

Wastewaters containing color, such as pulp and paper mill discharges, are sometimes even more difficult to treat than natural water sources. Experience and ingenuity are needed to screen potential coagulants; this is an area of water treatment that is still more an art than a science. An example of this was a study of a textile wastewater, where the color could not be removed by alum treatment followed by pH correction with alkali, but it could be treated by aluminate, followed by pH correction with acid.

Plant Design

For water clarification, water treatment plant designs are classified as either conventional clarification or direct filtration. A conventional clarification plant is capable of handling a wider range of impurities in influent raw water and usually involves sedimentation followed by filtration for raw water applications. Wastewater processes commonly use only sedimentation. Direct filtration is used when the incoming water does not contain many solids. A rule of thumb would be when influent is consistently greater than 10 NTU, sedimentation is cost-effective; less than 5 to 10 NTU can economically operate with only filtration. Both classes of water clarification plants can provide softening treatment, as necessary, using the lime softening process.

The design flow of a surface water clarification plant shows how the principles of coagulation and flocculation apply to actual plant design. Generally, the lower the suspended solids in the process stream, or the higher the required effluent clarity, the more critical is mixing to the final results. Surface water is relatively low in suspended solids, and removal to a low concentration of residual solids is usually required. For this reason, many water plants are designed with both flash mixing and flocculation mixing. The jar test protocol of rapid and slow mixing, which works best for raw water clarification, is duplicated on the plant scale. Flash mixing is accomplished in two ways: in-line hydraulic mixing (Fig. 6.15) and high-speed mixing in a small mixing basin (Fig. 6.16). The coagulant is added at or before the flash mix. Mixing can also be accomplished by hydraulic jumps in open channels, venturi flumes, and pipelines with tortuous baffles. However, these do not maintain the necessary *G* factor at low flows and are somewhat limited in application. In many situations, there is a practical benefit to having serial flash mixers (usually two) to improve coagulant dispersion, or to promote initial primary particle agglomeration. This has been especially useful in filter aid feed systems for maximum particulate removal and filter run length. Sequential flash mixing also provides flexibility in adapting to future plant requirements.

Flocculation mixing occurs in gently stirred compartments. Two common flocculator designs are the horizontal reel (Fig. 6.17) and the

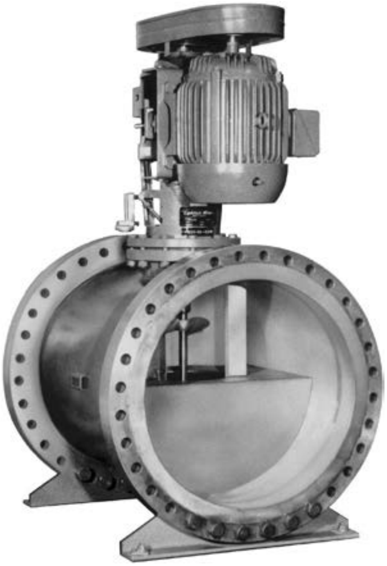


Figure 6.15 High-energy in-line mixer. (*Courtesy of Mixing Equipment Company.*)

Figure 6.16 Flash mixers are designed to disperse chemicals throughout the water instantaneously, before flocculation. (*Courtesy of FMC Corporation*.)

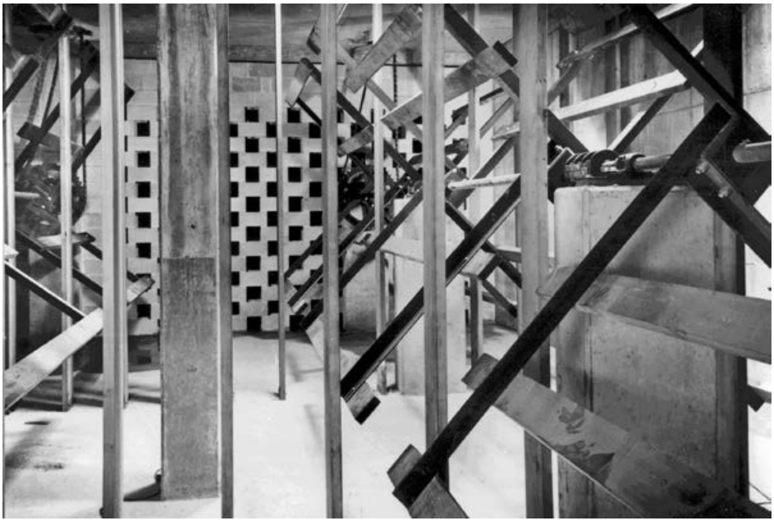


Figure 6.17 Reel-type paddle flocculator. (*Courtesy of Envirex, a Rexnord Company*.)

Figure 6.18 Turbine-type flocculators. (*Courtesy of Envirex, a Rexnord Company*.)

turbine mixer (Fig. 6.18). Variable speed motors may be provided to allow variation in mixing energy. Some plants employ hydraulic flocculation mixing, but this has limited use because the effectiveness decreases at reduced flows.

Silt or color removal in raw water is accomplished using two basic treatment schemes: conventional clarification or direct filtration. The most common plant operation is conventional with rapid mix, slow mix, sedimentation, and filtration (Fig. 6.19). Historically, alum has been most widely used, because the optimum pH is often

Figure 6.19 Conventional water treatment plant showing reel-type flocculation units, rectangular sedimentation basins in parallel with common wall construction, and sludge collection flights. Final filtration is not shown. (*Courtesy of FMC Corporation*.)

below 6. It is fed at the head of the plant, sometimes in conjunction with alkali for pH control. Iron salts are seldom used, since the optimum pH is greater than 7. Because alum floc is light, a polymeric flocculant is usually required to reduce carryover from the settling basin to the filters.

Polymer coagulants often are used to either replace or reduce inorganic salts. The polymer coagulant is added at the flash mix. Sometimes, alum can be replaced only if clay is fed to ensure high collision frequency, and to add weight to the floc. An alternate method is to return sludge from the bottom of the settling basin to the rapid mix. These methods essentially add solids to increase collisions. Adding solids can be beneficial during the initial startup of a clarifier. This increases agglomeration in low turbidity water and accelerates sludge blanket formation.

When the color or turbidity is very low in the raw water, direct filtration is often practiced. In a direct filtration plant, water passes through flash mixing, sometimes a flocculator, and then directly to the filters. There are so few solids in the water that the filters do not plug excessively. A polymer or a blend is used as the primary filter aid (coagulant) in this process, since inorganic salts add solids that could blind the filter.

High molecular weight flocculant polymers are not normally used as filtration aids because these excel at bridging, which is undesirable in the microscopic spaces between sand particles.

Wastewater streams usually have higher solids than raw water, and the required suspended solids removal may not be as stringent. Generally, for wastewater clarification, hydraulic mixing has been widely used in the past; but newer plants are being designed with mechanical mixing similar to raw water clarification plants, in order to improve removal of suspended solids.

Filtration

Water filtration is essentially a batch-type liquid-solids separation process for the removal of suspended material by passing it through a porous bed of sand or other granular materials. Granular media filtration is used to remove filterable solids from raw water, recycled water, floc particles from pretreated water, precipitates from the effluent of a lime or lime-soda ash process, iron and manganese precipitation products, and as a tertiary treatment step in wastewater treatment. Filtered suspended solids are usually removed from a filter by taking the filter out of service and backwashing the media, with the waste backwash water going to drain.

Granular media filtration, as used in water treatment, is generally applicable for removal of suspended solids in the 5 to 50 mg/L range, where an effluent of less than 1 NTU is required. Sand filters have been used for many years as a final polishing step in municipal and industrial water plants, where the clarifier effluent contains 5 to 20 mg/L of suspended solids. In areas where a very low turbidity raw water source is available, some water treatment plants use granular media filtration along with chemical conditioning as the only treatment process for solids removal, particularly for industrial process water. This is referred to as direct filtration.

Filtration Mechanisms

Granular media filtration is considered to include both physical and chemical mechanisms. Some particle removal, especially larger particles, may be considered mechanical straining, and as such, occurs mainly in the upper portion of a stratified media. For a granular media filter to remove other particles, especially smaller particles, these particles must be transported to a media grain and attach to that media grain or other particles previously deposited. Particle transport mechanisms within the media may include gravitational settling, interception, diffusion, hydrodynamic effects, and inertial forces.

Colloid chemical forces bring about particle attachment. As the particle approaches the media surface, or the surface of a previously deposited particle, the removal of that particle is dependent upon attachment mechanisms that may involve chemical bridging, specific adsorption, and electrostatic interaction. Increasing particle size enhances inertial impaction, hydrodynamic action, and gravity settling. Decreasing particle size enhances diffusion.

Figure 6.20 illustrates particle transport mechanisms. Gravity settling (a) is related to particle settling in the range of 2 to 10 µm. Diffusion (b) is related to Brownian diffusion for particles of 1 µm or

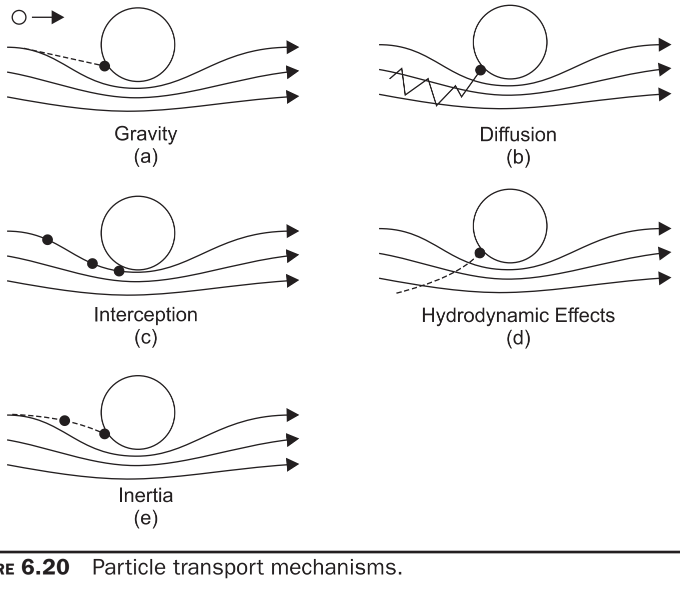


FIGURE 6.20 Particle transport mechanisms.

less. Interception (c) relates to the collision of a particle with the media. Hydrodynamic effects (d) relate to the crossing of fluid streamlines due to an existing shear gradient and impacting the media. Inertia (e) relates to a particle having a greater density than the liquid; this particle then experiences inertial forces, which cause the particle to cross the fluid streamlines before it flows past the media grain.

Usually a pretreatment step, often using a coagulant or flocculant, precedes filtration. If the floc particle is too large, it will blind (plug) the filter surface. If it is not properly treated or coagulated, it will completely pass through the filter. If the floc particle strength is too strong (Fig. 6.21), the service run may be shortened due to a high head loss. If the floc particle strength is too weak (Fig. 6.22), the service run may be shortened due to turbidity breakthrough.

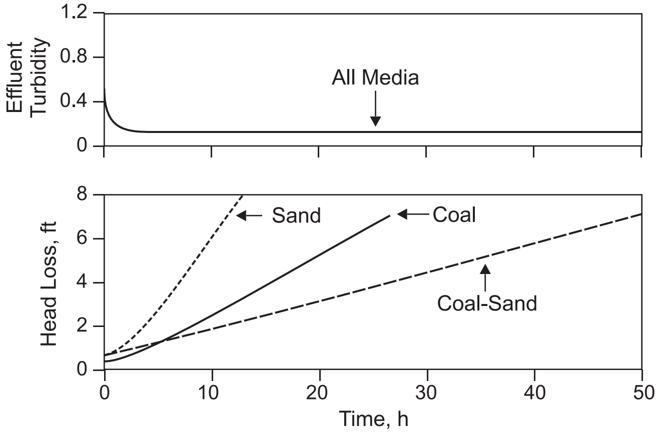


Figure 6.21 Strong floc effect on filter run length with various media.

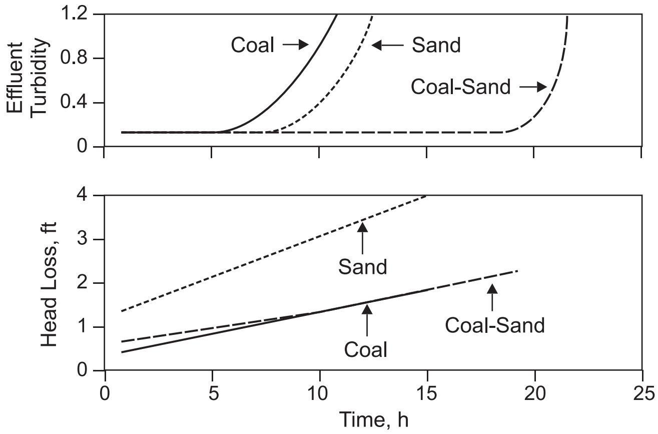


Figure 6.22 Weak floc effect on filter run length with various media.

Once the particles have contacted the media, they are retained by an attractive force. To remove these particles and those removed by straining, the filter bed is fluidized by upflowing the bed with water. The addition of an air scouring or surface wash agitation step in the backwash cycle greatly improves particle removal efficiency.

Granular Media Filters

Granular media filters are generally of the following three types:

- Gravity (conventional rapid sand, self-backwashing, or continuously cleaned)
- Pressure
- Upflow

The most widely used granular media filter in the municipal raw water treatment field is the conventional rapid sand type filter with either a single media (sand) or a dual media (anthracite-sand) bed. Pretreatment filters used in industry for large-scale applications are usually of the conventional type with dual media. Smaller industrial type filtration applications, such as boiler water pretreatment and recycle, are usually of the pressure filtration type.

Media, media depth, filter operational control method, backwash method, and underdrain design vary between the types of filters and within a type of filter. Therefore, a brief discussion of a conventional rapid sand filter configuration (Fig. 6.23), before highlighting the various filter types, will aid in understanding the operation of granular media filters.

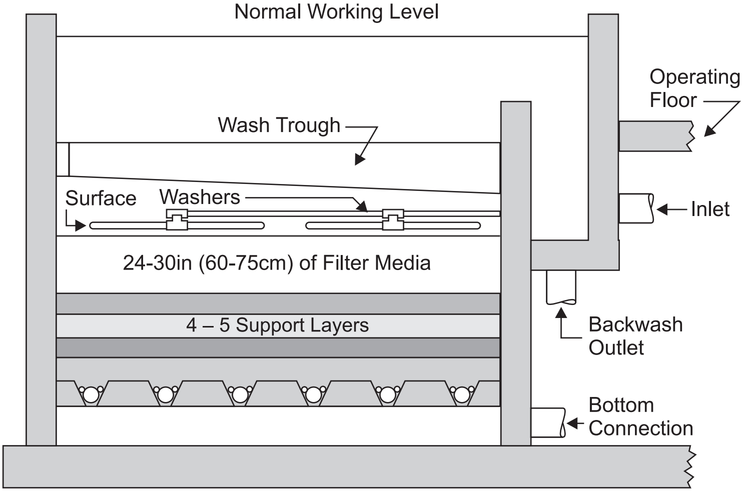


FIGURE 6.23 Conventional rapid sand filter.

The major portion of a filter configuration is determined by interrelated components such as filter area, filter depth, filter operational control method, backwash method, and to a minor extent the filter conditioning method, if used.

Filter area is determined by the actual flow rates expected and the selected design unit flow rate. The overall dimensions of a filter bay or cell are usually limited by the backwash water requirements such as storage, recovery, and the required backwash water rate.

Filter depth as measured from the top of the filter wall to the underdrain-supporting slab, provides for the necessary freeboard, submergence, media depth, and underdrain design.

Freeboard is as required by regulations or the plant hydraulic profile.

Submergence includes the depth of water provided for loss of head and the water depth required to prevent air binding in the media during a service run. Adequate submergence is also necessary to minimize inlet velocity above the filter bed surface. Note that part of the filter head loss includes the head loss through the underdrain system, including nozzles, effluent piping, and valves. The head loss through the underdrain system becomes critical if the unit filtration rate is increased substantially. Media depth and the underdrain system depth allowances are self-explanatory. Dual media and single media (stratified or unstratified) filters each have different depth requirements. The type of underdrain system selected has an additional gravel support bed depth requirement, ranging from none to several gradations of gravel. The placement of the wash water troughs or outlet above the media, depending upon the backwash water method used, determines any additional filter depth requirement for media expansion during the backwash cycle.

Operational control methods available are constant rate and variable declining rate. The filter configuration varies as to inlet and outlet structure, control valves, level sensing devices, etc., depending upon the control method selected.

In the constant rate mode, flow through the filter can be controlled by one of the following methods:

- Inlet flow, split between each filter cell, usually by means of weirs with a constant water level across the filter, maintained by an effluent line automatic throttling valve controlled by a level sensing device located in the water above the filter bed.
- Inlet flow, split between each filter cell, with the water level in each filter cell varying with the loss of head through the filter. An effluent weir arrangement properly positioned is usually provided for initial submergence of the media.
- Rate of flow controller in the filter effluent piping, to maintain a constant flow rate through the filter, by gradually opening up to a point, as the filter head loss increases.

Variable declining rate filtration operation requires multiple filter cells and results in a higher unit filtration rate (gpm/ft^2 or m^3/[h·m^2]) at the beginning of a service run than at the end of the service run. For this mode of operation, the water level is essentially the same in all operating filter cells at all times. As filtration continues, flow through the dirtiest filter tends to decrease, causing the influent flow to be redistributed to all filters automatically, so that cleaner filter cells pick up the capacity lost by the dirtiest filter cell. This method causes a gradual declining rate toward the end of a filter cell run. The advantage is that there is less hydraulic disturbance to the other filter cells in service, when a filter cell is taken off-line for backwashing, as that filter cell is already operating at a diminished proportion of the total inlet flow. Filter cells are generally cleaned on a selected time interval basis. Influent or effluent control (such as an orifice in the filtered water line) is used to restrict abnormally high unit filtration rates through a filter cell, when a cleaned filter cell is returned to service.

Storage capacity determines if the filtration system can be operated on a consistent basis in a true constant rate or variable declining rate mode.

Backwash methods in general vary, but the usual practice is to fluidize single (stratified) and dual media filters with an upflow of water to flush captured solids out of the filter. Auxiliary scouring devices such as surface washers or air scouring systems are frequently provided, especially with dual media filters, to remove impacted solids by increasing the number of collisions within the media.

Single media filters (unstratified) are simultaneously air-water backwashed at low subfluidizing backwash rates, followed by a low backwash water flow only. This method, used to flush out suspended solids and accumulated air, also keeps the media in the desired unstratified state, and is used in certain proprietary designs and deep bed filters.

Self-backwashing filters use on-line stored filtered effluent as the backwash water source, or when properly designed, the filtered effluent from the other filter cells in the cluster. Continuously cleaned filters usually use a central airlift device with baffles to clean a small portion of the media continuously and return the cleaned media to the top surface of the filter.

Filter conditioning is used to minimize the initial surge of filtered water turbidity that occurs when a backwashed filter is returned to service (Fig. 6.24). Methods used to overcome this initial water quality problem are:

- Filter to waste—piping arrangement
- Lower initial flow rate—instrumentation
- Polymer addition—chemical feed station

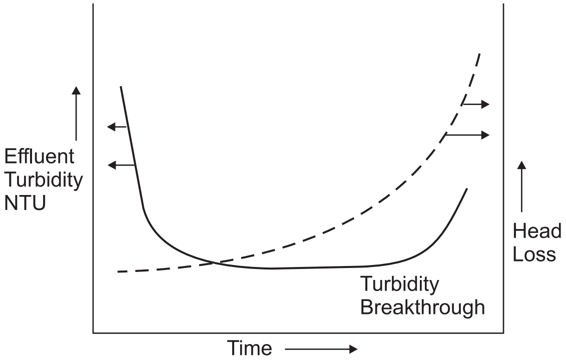


Figure 6.24 Filtered water turbidity and head loss profile versus time.

In filter to waste, the filtered water is wasted to drain until the desired quality is obtained. This method has the disadvantage of contributing to waste water volume. The lower initial flow rate method involves slowly opening the filter service valve over a period of time, until the filter bed is hydraulically stabilized with regard to suspended solids retention. Disadvantage is loss of full service flow for a period. Polymer addition during the last few seconds of a backwash conditions the filter media to retain suspended solids. This is an effective and flexible method to condition a filter.

Conventional Rapid Sand Filter

Figure 6.23 shows a gravity filter of the conventional rapid sand type. The great majority of municipal water treatment plant filters are of this type.

Water enters the filter through the influent valve, passes through the filter bed, collects in the filter underdrain, and is discharged through the effluent valve. The filtered water flow is controlled by an effluent rate of flow valve. At the start of a backwash cycle, the water level is drained to within a few inches (millimeters) of the surface sweep arms. The drain valve is closed, the backwash wastewater valve is opened, and the surface wash is initiated.

After sufficient scouring occurs, the surface wash system is stopped. The backwash water supply valve is opened, and the water flows up through the bed at a rate high enough to fluidize the bed and dislodge accumulated solids. Backwash water overflows the wash water trough and flows to drain. The backwash water rate is much higher than the service flow rate for this type of filter. Backwashing usually takes 8 to 15 minutes or until the waste backwash water runs clear.

Granular Media Filter Beds

Granular media bed classifications include the media composition and arrangement, media size distribution, and filter depth. Common

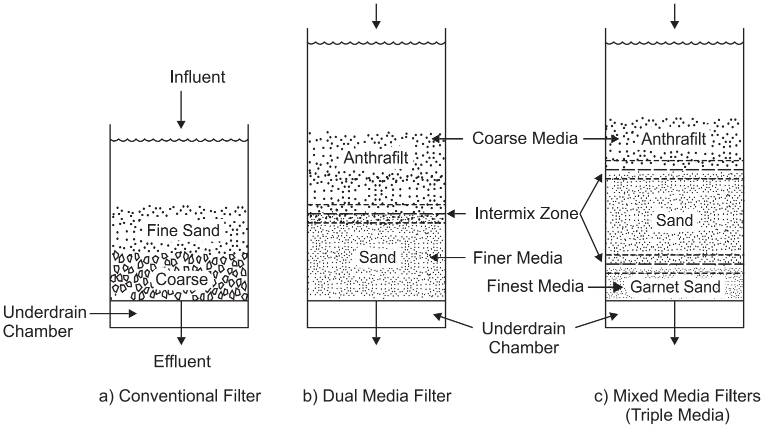


FIGURE 6.25 Filter media compositions and arrangements.

media compositions and arrangements used in water filtration (Fig. 6.25) include single media (a), using either sand or anthracite; dual media (b), using anthracite and sand; and mixed media (c), using anthracite, sand, and garnet.

The heights of the intermix zones, shown in Figs. 6.25*b* and *c*, are dependent in part on each media's effective size (ES) and uniformity coefficient (UC).

The UC characterizes the fine and coarse grain distributions in the media, and is by definition the 60% size divided by the 10% size. The ES by definition is the 10% size. Sizes are determined by plotting on log normal probability paper, the cumulative weight percent of the media retained on various US standard sieves versus the separation size (mm).

The intermix zone occurs because the larger size anthracite in the lower portion of the stratified anthracite bed mixes with the finer sand in the upper portion of the stratified sand bed. Media grain size distributions for the various media compositions and arrangements are illustrated in Fig. 6.26.

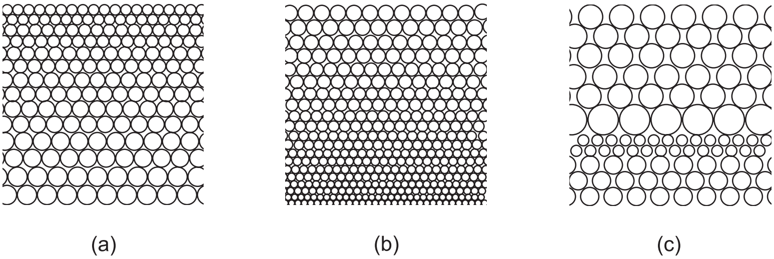


FIGURE 6.26 Media arrangements and grain size distributions.

By using larger media particle sizes of a lower density than the succeeding layer, the general media gradation for filter beds (Figs. 6.26*b* and *c*) can be made coarser-to-finer, as opposed to the media bed shown in Fig. 6.26*a*, which is finer-to-coarser.

The advantage of a coarse-to-fine grain distribution, or a uniform grain size distribution, is that of in-depth filtration [filtration across the majority of the media depth rather than filtration just in the first few inches (millimeters)] of the bed, as is characterized by the grain size distribution of the stratified filter bed of Fig. 6.26*a*.

Depth of the media plays a part in effluent turbidity along with the media ES. The depth of the anthracite layer in a dual media filter provides storage for the coarser particles in the water, before final polishing by the lower finer sand bed. The unstratified bed acts in a similar manner, with solids captured across the depth of the bed rather than just in the upper few inches (millimeters) of a stratified sand bed or in the anthracite media, as in a dual media filter.

Figures 6.21 and 6.22 graphically illustrate the preceding discussion. The media are sand [0.45 mm E.S., 2 ft (0.6 m) deep]; coal [0.7 mm E.S., 2 ft (0.6 m) deep]; and dual media [coal: 1.05 mm E.S., 1.5 ft (0.5 m) deep] and sand [0.45 mm E.S., 0.5 ft (0.15 m) deep]. Clarifier effluent turbidity for the strong floc was 2 NTU, while that for the weak floc was 15 NTU.

Figure 6.21 shows the effluent turbidity for all arrangements being the same. This would be so, since the sand media is the same in the sand filter and the dual media filter. An ES of 0.7 mm anthracite approaches a 0.5 mm ES characteristic, because of the irregular shape of the anthracite. Head loss was higher for the sand media because of the initial solids capture in the first few inches (millimeters) of the stratified sand bed as previously discussed. Head loss for the coal media was greater than the dual media filter, because of the finer coal size used in the coal media filter.

In Fig. 6.22, effluent turbidity was greater for the coal filter, because of its larger pore size versus the smaller pore size in the sand filter. The dual media filter provided greater storage of the floc in the anthracite layer and finer polishing in the sand layer.

Head loss for the sand filter is greater, because of greater capture of solids. Equal head loss for the coal filter and the dual media filter reflects, in part, loss of solids through the anthracite filter, as evidenced by higher effluent turbidity.

Both Figs. 6.21 and 6.22 illustrate the overall effects that must be reviewed when considering backwash initiation on a turbidity, time, or head loss basis, using various types of filter media and treated influent water characteristics.

Filter Backwashing Systems

A filter bed can function properly only if the backwashing system used in conjunction with the filter design effectively cleans the material removed by the filter. The methods commonly used for backwashing granular media filter beds include:

- Water backwash only
- Water backwash with auxiliary surface wash
- Water backwash with auxiliary air scour
- Combined air-water backwashing

Note that the specific application of one of these methods to a filter depends upon the filter configuration, filter control, media, etc. as previously discussed.

> *Water backwash only*—The idea in the system using water backwash only is to fluidize the filtering media, so that the shearing action of water as it moves past individual grains scours material that has accumulated. These systems have been used in water treatment plants, where solids and turbidity levels are relatively low.
>
> *Water backwash with auxiliary surface wash*—Surface washers can be used to provide extra shearing force to improve cleaning of the grains. Operationally, the surface washing cycle is started for about one or two minutes after the water level is drained to the recommended level above the centerline of the surface sweep pipe arms. Then the backwash flow is started, and both cycles are continued for about two minutes, at which time the surface wash is terminated. Water usage is as follows:

- For a single-surface sweep backwashing system: 0.5 to 1 gpm/ft^2 (1.2–2.4 m^3/[h·m^2])
- For a combined surface sweep-subsurface backwashing system: 1.5 to 2 gpm/ft^2 (3.7–4.9 m^3/[h·m^2])

> *Water backwash with auxiliary air scour*—Operationally, air is usually applied for three to four minutes after the water level has been drained to the recommended level above the media surface and before the water backwashing cycle begins. Typical airflow rates range from 3 to 5 cfm/ft^2 (0.9–1.5 m^3/[min·m^2]). Because of the violent action of the air injected into the filter bed, conventional gravel underdrain systems cannot be used without additional restraints. Therefore, when air scour is used, the filtering medium is placed directly on a specially designed underdrain system. (See discussion of underdrain systems later in this chapter.)
>
> *Combined air-water backwash*—The combined air-water backwash system is used in conjunction with the single media unstratified filter bed. Operationally, air and water (at a low rate) are applied simultaneously for several minutes. The specific duration of the combined backwash varies with the design of the filter bed. At the end of the combined air-water backwash, a two to three minutes

water backwash at subfluidization velocity is used to remove air bubbles that remain in the filter bed. This last step is required to eliminate air binding within the filter.

Backwash water rates are dependent upon the media size, media type, backwash water temperature, and the type of filter backwash water system used, along with the filter configuration provided. The manufacturer's instruction book or the treatment plant's operation and maintenance manual should be consulted before changing an existing backwash water flow rate.

Filter Appurtenances

The principal filter appurtenances are:

- The underdrain system is used to support the filtering materials, collect the filtered effluent, and distribute the backwash water and air (where used).
- The wash water troughs are used to remove the backwash water from the filter.
- The surface washing systems, when used, help remove attached material from the filter media.

Underdrain systems—The type of underdrain system used depends on the type of backwash system. In conventional water backwash filters without air scour, it is common practice to place the filtering media on a support consisting of several layers of graded gravel and a coarser media layer. When there is to be a gravel layer, an underdrain system, such as the one shown in Fig. 6.27, is used. With air scour or combined air-water backwash systems, there is usually no gravel layer, and underdrain

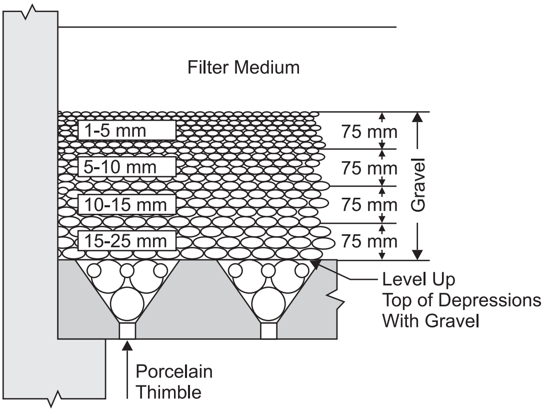
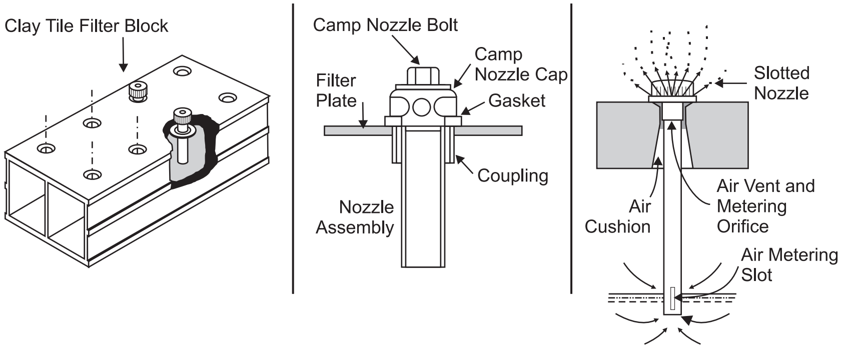


Figure 6.27 Filter underdrain systems with gravel sublayers.



Clay Tile

Campwalker Filter Underdrain System

Airwater Nozle Underdrain System

Figure 6.28 Underdrain nozzles used in filters without gravel sublayers.

systems of the type shown in Fig. 6.28 are generally used. In the single-media unstratified filter bed, the grain size is sometimes larger, and the slot or screen size in the backwash nozzle can be larger.

Wash water troughs—Wash water troughs are now constructed of plastic, sheet metal, or concrete with adjustable weir plates. The particular design of the trough depends to some extent on the other equipment used in the design and construction of the filter.

Surface washers—Surface washers for filters can be fixed or mounted on rotary sweeps. According to data on a number of systems, rotary-sweep washers are the most effective.

Service Operating Parameters

Filters are designed and operated based on hydraulic loading or filtration rate expressed as gpm/ft^2 [m^3/(h·m^2)]. The parameter can be calculated from Eq. (6.8):

$$\text{Filtration rate} = F/A \tag{6.8}$$

where filtration rate = hydraulic loading, gpm/ft^2 or m^3/(h·m^2)
F = filter water flow rate, gpm or m^3/h
A = filter surface area, ft^2 or m^2

Normal operating rates vary with the type of filter system used (gravity or pressure filters). Unit filtration rates for conventional water treatment rapid sand type filters, are generally 2 to 4 gpm/ft^2 [4.9–9.8 m^3/(h·m^2)].

Normal operation is judged by two variables: quality of water produced and length of filter run. A time profile of turbidity (the measure of water quality) and head loss provides a picture of filter operation. Figure 6.21 shows typical changes in water quality when operating a filter at a constant rate over time. When the filter is first brought into service, relatively high turbidity is encountered in the filtered water. Filter conditioning can last from five minutes to two hours before turbidity drops and stabilizes. After a length of time, the turbidity rapidly increases. This sudden increase (turbidity breakthrough) occurs when the shear forces in the filter, which increase as head loss increases, become greater than the shear strength of the trapped floc. During the filtration process, head loss builds as shown in Fig. 6.21. There may be no correlation between breakthrough and head loss; breakthrough can occur at high or low head loss. If there is a sudden increase in influent flow to the filter, previously captured suspended solids may slough off the media and pass through the filter bed, thereby causing a higher effluent turbidity until the filter bed hydraulically restabilizes.

Water Quality

Turbidity or suspended solids in the filter effluent are the primary measure of filter efficiency. The effluent turbidity actually depends on the turbidity removal efficiency of the filter. The efficiency expressed as a percent is calculated using Eq. (6.9):

$$E = (100)(\mathrm{TSS}_I - \mathrm{TSS}_E)/\,\mathrm{TSS}_I \tag{6.9}$$

where E = removal efficiency, %

TSS_I = influent suspended solids, mg/L

TSS_E = effluent or filtrate suspended solids, mg/L

Effluent turbidity can be affected in two ways:

1. If filtration removal efficiency remains constant, a change in influent turbidity affects effluent turbidity.
2. If influent turbidity remains constant, a change in filtration removal efficiency affects effluent turbidity.

Most filtration operations run with at least 70% removal efficiency.

Many factors can affect influent turbidity; some are controllable, and some are not. If a clarification program precedes filtration, changes in the chemical or mechanical program can change the amount and nature of the incoming suspended solids. If no sedimentation type pretreatment step is present, there may be little that can be done to change the volume of influent solids.

The efficiency of the filter is also influenced by many factors, a number of which are controllable. Factors affecting filtration efficiency are:

Filterability of suspended solids—Colloidal solids are not readily filterable, because they are not easily adsorbed on the filter media. Other floc particles, such as alum floc, may be too large and tend to blind filter media. The strength of the floc trapped in the void spaces also affects turbidity removal efficiency. Chemical and mechanical changes before filtration can affect floc filterability.

Type of media—The finer the media, the higher the efficiency. Generally, a mixed-media or dual-media filter is more efficient than a single-media filter, especially as filtration rates increase.

Physical condition of the media—If some of the media is missing or if it is dirty after backwashing, efficiency decreases.

Chemical conditioning of the media—The surfaces of the media are charged; just as colloidal particles are charged. Generally, if the media is positively charged by cationic polymer addition, electrokinetic forces of attraction exist between the media surface and the floc particles, enhancing solids capture.

Flow rate—As the flow rate increases, the possibility of floc passing through the filter also increases.

Changes in flow rate—Any increase in flow rate disturbs the floc accumulated in the bed. Some flocs are shear sensitive and are dislodged during flow changes.

Length of filter runs—The other major measure of filter operations is length of filter runs. Filter runs are measured by the number of hours the filter is on line, although gallons (m^3) of water produced are a better measure. A filter operating for 20 hours at 5 gpm/ft^2 [12.2 $m^3/(h \cdot m^2)$] processes more water between backwashes than one operating for 30 hours at 3 gpm/ft^2 [7.3 $m^3/(h \cdot m^2)$]. Another measure is the percentage of treated water required to backwash filters. A well-operated plant uses less than 3% of its treated water for backwash. It is desirable to extend filter runs, since backwashing can be expensive in terms of personnel, water usage, and electrical cost.

A filter is backwashed for three reasons:

1. *Breakthrough occurs*—Where effluent turbidity standards govern, particularly in municipal plants, turbidity breakthrough rather than time or head loss is the main criterion for backwash initiation.
2. *Head loss exceeds maximum desired level*—When pressure drop exceeds some predetermined level, the filter is backwashed. Usually, this level is determined by experience, so that the filter is backwashed before turbidity breakthrough occurs.

3. *Time*—Many plants, particularly industrial plants, arbitrarily choose to backwash filters at a convenient interval, usually every 24 hours or once per shift. They find that water quality is maintained at an acceptable level, while providing a defined procedure for shift operators.

Filter run length is affected by several variables. The factors affecting turbidity breakthrough have already been discussed. Head loss is most commonly affected by the volume of solids in the influent water. The more influent suspended solids, the shorter the filter runs. The nature of the solids and the coagulation program used in pretreatment, as discussed before, may result in a floc that is so large or adhesive that it blinds the surface, causing rapid head loss. The deeper the average floc penetration into the bed, the less head loss for a given volume of floc removed. Dual and mixed-media filters give longer filter runs, since the coarse material is stored in the top anthracite layer and the finer material stored in the finer sand layer.

The cleaner the bed after backwash, the lower the initial head loss, and a clean bed can accumulate more solids before reaching the maximum head loss.

Chemical Treatment

Chemical treatment in raw water filtration can be accomplished by any of several techniques. Coagulants and flocculants can be added as filter aids to improve the filtration process. Generally, coagulants are used in direct filtration chemical treatment for process performance improvement. Chemical cleaner programs can be used on media during or before backwash, to reduce solids retained in or on the filter media in the backwash cycle and to improve overall treatment performance.

Filter aids are chemical treatments for improving filter efficiency. The most common application, and what is usually meant as a filter aid, is the continuous feed of polymer, either a flocculant or a coagulant, at low dosage directly to water going to the filter. A second application is to the backwash water to aid filtration during the first minutes that the unit is on stream. Figure 6.29 shows effluent turbidity during a filter run with and without a filter aid. With addition of a filter aid, filter turbidity comes down faster after backwash, reaches a lower level, and breakthrough is postponed. Lower average turbidity during the run indicates the filter aid has increased filtration efficiency.

Two types of products are used as filter aids:

1. Coagulants
2. Flocculants

Generally, coagulants are used since they are easier to feed. In addition, they provide more flexibility if the turbidity coming to the

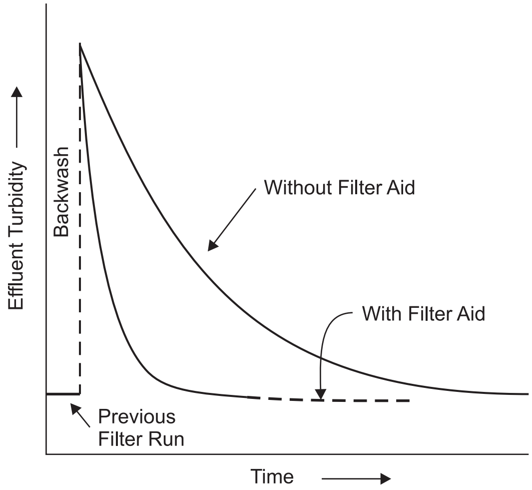


Figure 6.29 Filter efficiency improvement with filter aid.

filter is under-coagulated, since the coagulant neutralizes the charge and increases removal. Coagulants are fed at 0.25 to 1 mg/L as filter aids. Over feeding can cause filter blinding. Filter aids can be fed dilute or as concentrated as 30%. In some cases, solution application strength toward the more concentrated levels improves performance.

High molecular weight flocculants work by strengthening floc trapped in the filter, thus improving shear sensitivity. Flocculants are fed at lower dosages of 10 to 100 μg/L and provide better shear resistance and economics but are more difficult to handle than coagulants. Overdosage of flocculants quickly causes filter blinding.

Flocculants can be used, if the filter is experiencing breakthrough without high loss of head. If the filter is experiencing both breakthrough and high head loss, a flocculant should not be used as a filter aid, because head loss will increase even more. In this case, the better choice is a coagulant. Flocculants must be fed at very dilute solution concentrations, because of the low dosages required. Feed at the same location as indicated for a coagulant.

To bring filters on-line faster (reduce initial turbidity faster), a coagulant can be fed to the filter backwash water. This can be done as a quick test to show the activity of a coagulant as a filter aid and filter conditioner. Be careful when applying this slug feed, if ion exchange units follow filtration, because cationic coagulants can foul cation resin.

Direct Filtration

Direct filtration lacks a precise definition, but in general it means that the overall treatment process does not include a sedimentation step prior to filtration and that all of the raw water suspended solids plus those added by treatment chemicals must be stored in the filter during its service run.

This definition would include those direct filtration plants, where coagulant is added to untreated raw water upstream of the filter and where definite rapid mix and flocculation stages precede the filter. It would also include those plants with separate rapid mix and flocculation steps ahead of a grossly hydraulically overloaded clarifier and those plants where low seasonal raw water turbidity either allow the settling function to be taken out of service or render the clarifier nonfunctional.

With separate coagulation and flocculation stages, chemical conditioning is targeted toward obtaining a floc designed to penetrate the filter bed in-depth and to resist shear forces. In other words, neither a strong floc nor a weak floc is desired.

In direct filtration where the coagulant is added upstream of the filter, the filter can be considered as a reactor with the chemical with physicochemical reactions occurring within the media bed.

The direct filtration potential for any raw water is related to the amount of chemical treatment required to destabilize the turbidity and color, so that they can be reduced by filtration to meet required levels. The method of determining the direct filtration potential of raw water is jar testing to determine a workable chemical program, followed by a No. 40 Whatman paper filtration test to determine the optimum chemical dosage and filtered water turbidity. If the results warrant, pilot plant testing is conducted.

Direct filtration is most suited for raw waters that seldom exceed 5 NTU turbidity or 20 APHA color, although higher levels can be handled, especially in industrial plants where maximum turbidity or color removal is not required. Upflow filters can handle much higher levels, but are generally used only in industrial plants.

Even though a conventional filtration plant may have some design limitations for direct filtration, such as mixing and filter media, conventional plants have flexibility not available in a direct filtration design. Having flocculation and a sedimentation basin available can be a great advantage. The flocculator can provide additional mixing, which may improve direct filtration results. In addition, the plant can return to conventional operation, when raw water turbidity and color increase. In most cases, even in direct filtration operation, some floc is removed across the basin, reducing load on the filters.

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CHAPTER 7

Ion Exchange

For as long as water has been used in industrial processes, deposits from undesirable ionic species have been precipitating on equipment. Deposits result in reduction in heat transfer at a minimum, and up to and including catastrophic loss at the extreme. Some of the earliest attempts to remove undesirable ions occurred with the use of naturally occurring inorganic sodium aluminosilicates. Much has changed since the early years of ion exchange. This chapter explores various synthetic ion exchange resins and the mechanical systems that are in use to shape ionic characteristics of water, in order to minimize operational problems in target water systems.

While the ion exchange system is often named for its equipment configuration, it is the resin contained within the vessels that governs the changes in water chemistry. Water quality at the vessel outlet is primarily a function of the type of resin and regenerant utilized, and secondarily how the equipment is performing.

The ion exchange process is exactly that, an exchange of one ion for another, utilizing a synthetic resin in order to accomplish transfer. As water passes through resin, ion exchange occurs, removing targeted ions from the water and replacing them with more desirable ions that have been loaded on the resin. Which ions are loaded on the resin and which ions are exchanged are determined by the regenerant used and the type of resin loaded in the vessel. The process is reversible, meaning that the resin bed can be recharged once exhausted. Recharging the bed is accomplished through a process called regeneration.

Ion Exchange Resins

Synthetic ion exchange resins are a copolymer of divinylbenzene (DVB), and styrene or acrylic polymers. When these are reacted chemically during manufacture, they achieve desired ion exchange characteristics and properties. Finished resin is comprised of small, insoluble, and permeable beads of varying particle sizes. Each bead contains water that makes up approximately 50% of the bead's weight. During the manufacturing and activation process, each resin is given either cation or anion exchange properties by permanently locking positively or negatively charged exchange sites into the polymer skeleton. The styrene skeleton of the resin bead is a wraparound structure much like a ball of twine. Water flows not just over the surface, but also through the permeable bead. Since exchange sites are all along the skeletal structure, both inside and outside the bead, exchange capacity is significantly higher than if just the external surface of the bead exchanged ions.

Cation resin exchanges desirable cations to the water from negative permanent sites on the resin; anion resin exchanges desirable anions to the water from positive permanent sites. Thus, resins are named for ions they exchange, not charges on the resin itself. Figure 7.1 illustrates a cation exchange resin. Negatively charged permanent sites are loaded with the sodium cation ready to exchange.

These permanent sites are capable of retaining ions of opposite charge taken from the surrounding water. Ion exchange is reversible, and ions removed from water can be regenerated, or displaced, from

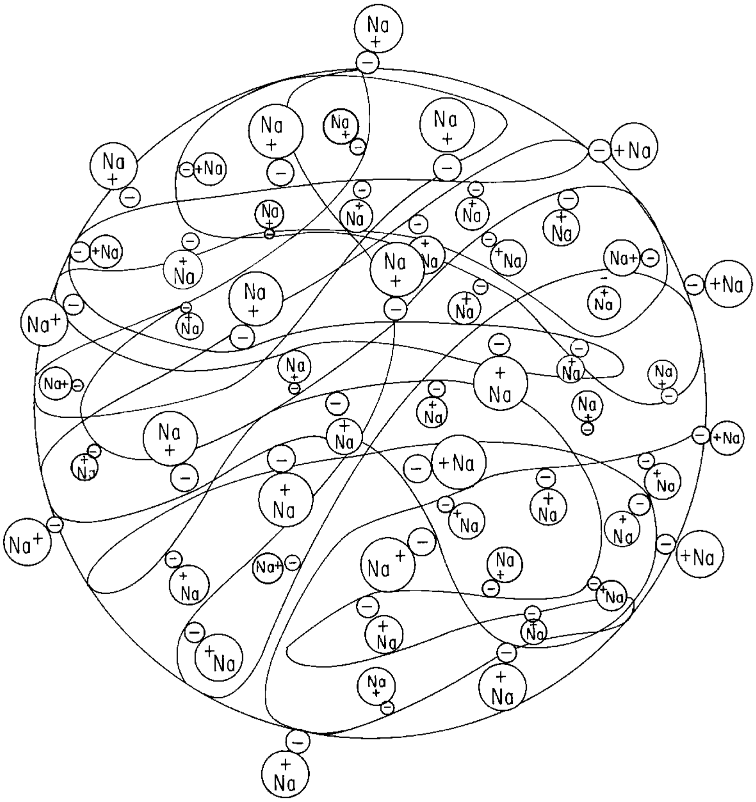

Figure 7.1 Illustration of cation exchange resin showing negatively charged exchange sites holding sodium ions.

resin by contact with a solution containing other ions of similar charge. Ions released or eluted from resin sites are discharged to waste during the regeneration process. Equation (7.1) illustrates the exchange process of a strong cation resin in sodium form, exchanging sodium ions for calcium ions.

$$2\text{RNa} + \text{Ca(HCO}_3)_2 \xrightarrow{\text{flow}} \text{R}_2\text{Ca} + 2\text{NaHCO}_3 \tag{7.1}$$

where R = active ion exchange site on resin (single valence)
2RNa = resin charged with sodium available to exchange other cations
R_2Ca = resin with calcium exchanged for sodium

Ion Affinity

Resin affinity is a reflection of relative selectivity for ions by resins. Generally, affinity is strongest with higher valence and higher atomic mass (Fig. 7.2). There are exceptions to these general rules, particularly with ions that form complexes or insoluble compounds, such as high molecular weight organic acids for anion exchange resins.

Resin Bead Structure

A combination of both the chemical and physical structures govern to some degree or another, kinetics, capacity, strength, and life span of resin beads.

Chemical Structure

Two basic chemical structures used in the manufacture of resins are styrene and acrylic acid. Styrene-based materials are aromatic hydrocarbons, while acrylic-based resins are straight-chained hydrocarbons based on polyacrylate or polymethacrylate. However, resins of both types use DVB as a cross-linking agent to physically strengthen the resin beads.

Strong acid cation (SAC) exchange resins are styrene, and their exchange sites are derived from sulfonic acid (H_2SO_3). Weak acid cation (WAC) exchange resins are acrylic, and their exchange sites are carboxylic acid (–COOH).

Strong base anion (SBA) exchange resins may be either styrene or acrylic based. Styrene-based materials receive their functionality from quaternary ammonium exchange sites. Type I resins differ from Type II in that the amine used for chemical activation in Type I resins has three methyl groups, while the amine used in Type II has one ethanol and two methyl groups. Weak base anion (WBA) exchange resins may be either styrene or acrylic-based materials.

Physical Structure

There are two physical structures in ion exchange resins based on styrene: gel and macroporous. Gel is the most common structure, which is a homogeneous crosslinked polymer in which exchange sites are

Cations	Anions	Affinity
Fe^{+3}	CrO_4^{-2}*	Highest
Al^{+3}	SO_4^{-2}*	↓
Pb^{+2}	SO_3^{-2}*	
Ba^{+2}	HPO_4^{-2}*	
Sr^{+2}	CNS^-	
Cd^{+2}	CNO^-	
Zn^{+2}	NO_3^-	
Cu^{+2}	NO_2^-	
Fe^{+2}	Br^-	
Mn^{+2}	Cl^-	
Ca^{+2}	CN^-	
Mg^{+2}	HCO_3^-	
K^+	$HSiO_3^-$	
NH_4^+	OH^-	
Na^+	F^-	
H^+		
Li^+		Lowest

*These ions may be displaced as they are protonated at low pH to $HCrO_4^-$, HSO_4^-, HSO_3^-, and $H_2PO_4^-$.

Figure 7.2 General order of ion selectivity in water below 1000 mg/L total dissolved solids (TDS).

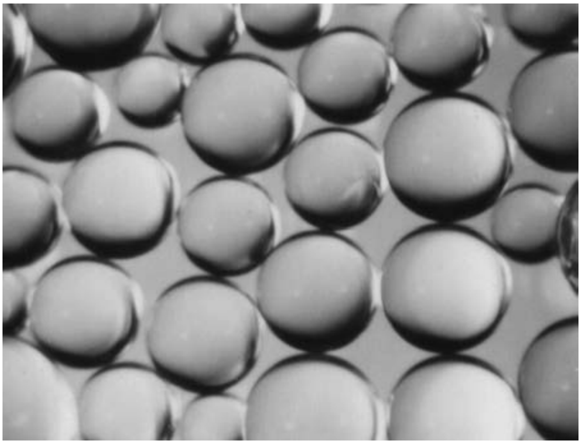

Figure 7.3 Typical gel resin (magnified).

distributed evenly throughout the bead. Physical strength of gel resins depends on the percentage of DVB cross-linking used in the manufacturing process. Standard SAC resins use 8% cross-linking; this is the most common cation resin and the one used in water softening applications. However, additional physical strength is gained by increasing cross-linking percentage, with an upper limit of 20%. Increased strength generally comes at the expense of slower kinetic exchange rates, lower exchange capacity, and higher cost. Gel resins are generally translucent in appearance (Fig. 7.3).

A macroporous (sometimes referred to as macroreticular) bead structure provides harder and stronger resins more resistant to oxidative and physical stress attack. Unlike gel resins, macroporous resins have a definite pore distribution in a sponge-like formation. Because of the pores in the active portion of the polymer, very high percent cross-linking is possible, but manufacturers do not state the actual percentage. Pores can constitute 10 to 30% of the bead volume, which causes a proportionate reduction in ion exchange capacity. Macroporous resins are typically opaque (Fig. 7.4).

Particle Size and Size Distribution

Historically used manufacturing processes resulted in resin bead particle sizes ranging from 16 to 50 mesh (1.19–0.30 mm) and a uniformity coefficient of 1.5 to 1.7, with the majority of beads being in the center of a typical Gaussian bell curve.

To optimize service and regeneration of ion exchange operations, a special process that results in more than 90% of beads being the same mesh size produces a newer class of resins. Such resins are called uniform particle size (UPS) resins (Fig. 7.5). During service, exchange kinetics are optimized because film diffusion is

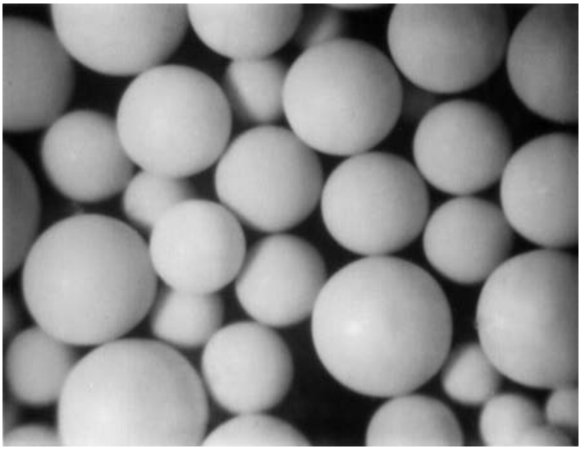

Figure 7.4 Typical macroporous resin (magnified).

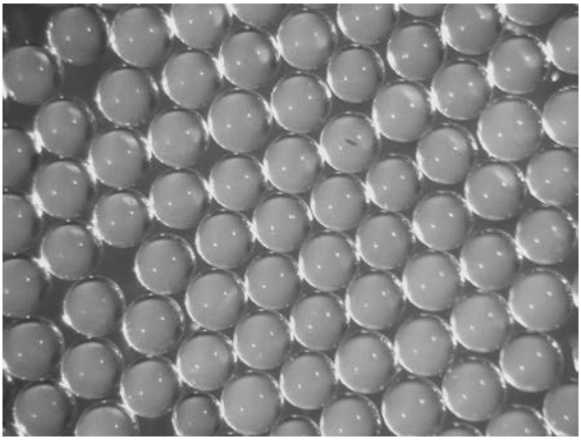

Figure 7.5 Uniform particle size (UPS) resin (magnified).

the controlling rate, and the consistent surface area per unit volume in UPS beads facilitates this principle. In the rinse step, particle diffusion is the controlling rate, and with UPS resins, the longer rinse time and larger waste volume required to rinse large beads is eliminated. Figure 7.6 illustrates this concept. Observed advantages are higher regeneration efficiency, increased operating capacity, and reduced rinse volumes. In mixed bed demineralizers, where the effectiveness of the separation backwash is a key to regeneration success, separation is improved because the UPS beads are more precisely engineered. As a result of this a 1980s innovation of using an inert resin layer to facilitate cation and anion bead separation is more rarely seen now.

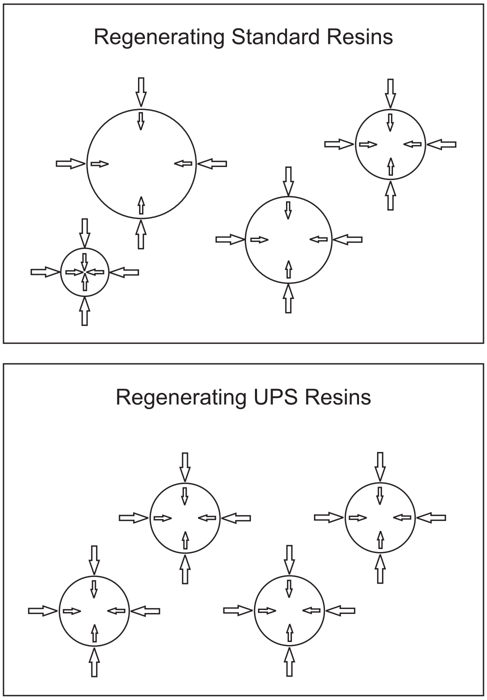

Figure 7.6 Regeneration difference between standard resin and UPS resin.

Resin Capacity

Units for expressing resin capacity are equivalents per liter (eq/L), milliequivalents per milliliter (meq/mL), kilograins per cubic foot (kgr/ft^3), and grams per liter (g/L). Generally, chemists use the first two units; the last two are practical units used by designers, engineers, and system owners.

When calculating the ionic load for resin, individual ions must first be expressed as their calcium carbonate ($CaCO_3$) equivalents in terms of mg/L. Applicable ions are then totaled and converted to ionic load expressed as grains per gallon (gr/gal) or grams per liter (g/L). Table 7.1 shows conversion factors to express ionic concentration in $CaCO_3$equivalents.

A typical raw water analysis expressed as $CaCO_3$ equivalents allows determination of several items that are important in understanding the ionic load that needs to be removed through ion exchange. Total cations (TC) is the sum of all cations present including calcium, magnesium, sodium, potassium, and any others found through analysis to be significant. Total hardness (TH) is a subset of TC and is just the sum of calcium, magnesium, barium, and strontium ions.These are the targeted species for removal with softener operation. Calcium and magnesium ions are the major hardness concerns.

Ion	Expressed as	Multiply by for $CaCO_3$ Equivalent
Barium	Ba^{+2}	0.78
Strontium	Sr^{+2}	1.14
Calcium	Ca^{+2}	2.50
Magnesium	Mg^{+2}	4.12
Potassium	K^+	1.28
Ammonia	NH_3	2.94
Sodium	Na^+	2.18
Carbonate	CO_3^{-2}	1.67
Sulfate	SO_4^{-2}/Na_2SO_4	1.04/0.70
Nitrate	NO_3^-	0.81
Chloride	$Cl^-/NaCl$	1.41/0.85
Bicarbonate	HCO_3^-	0.82
Hydroxide	OH^-	2.94
Fluoride	F^-	2.66
Carbon dioxide	CO_2	1.14*
Silica, reactive	SiO_2	0.83*

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*These values are for ion exchange applications only and are one-half the values used for lime softening calculations.

Table 7.1 Calcium Carbonate Conversion Factors for Common Ions

Total anions (TA) is the sum of all anions present including alkalinity, chloride, sulfate, nitrate, and any others found through analysis to be significant.

Once TC and TA are known, ionic load can be determined by evaluating which ions are removed through the ion exchange process. Total exchangeable cations (TEC) is the sum of all cations removed by cation resin. Total exchangeable anions (TEA) is the sum of anions removed by anion resin. For SBA resin, the TEA number includes carbon dioxide (CO_2) and silica (SiO_2). For WBA resin, carbon dioxide and silica are not included in the TEA calculation.

The total exchangeable ions definition can change depending on resin type and regenerant chemical used. For instance, SAC resin in the sodium form SAC (Na^+) only exchanges sodium for TH (Ca^{++}, Mg^{++}, Ba^{++} and Sr^{++}), while the same resin operating in the hydrogen form SAC (H^+) also removes sodium, potassium, and any other cation present. Table 7.2 is a typical raw water analysis showing TH, TC, and TA.

Constituent	Concentration*
Calcium	194.0
Magnesium	70.2
Sodium	14.4
Potassium	1.5
Total hardness (TH)	264.2
Total cations (TC)	280.1
Bicarbonate	220.0
Chloride	5.2
Sulfate	54.0
Nitrate	0.9
Total anions (TA)	280.1
TMA[†]	60.1
P alkalinity	—
M alkalinity	220
Carbon dioxide, CO_2	11
Silica (reactive), SiO_2	0.7
TDS, mg/L[‡]	428
Conductivity, μS/cm	564
pH, units	7.6

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[*] All mg/L as $CaCO_3$ except if noted otherwise.
[†] Theoretical mineral acidity (sum of anions less alkalinity, carbon dioxide, and silica).
[‡] Total dissolved solids.

Table 7.2 Raw Water Analysis Indicating Total Hardness, Total Cations, and Total Anions

Ionic loading for resin is expressed as mass per unit volume. Typical conventions are grains per gallon (gpg) in U.S. units and g/L (or mg/L) in metric units. Using the data in Table 7.3, this raw water has a TH ionic load of 15.45 gpg or 0.2642 g/L for a SAC (Na^+) unit and a TC ionic load of 16.38 gpg or 0.2801 g/L for a SAC (H^+) unit.

The theoretical exchange capacity of any given resin is a design feature based on brand and resin type. Practical or use capacity varies based on a variety of factors including regenerant mass and concentration, resin degradation, and fouling to name a few. Resin specifications list capacity based on type and dosage of regenerants. Capacity is expressed in kgr/ft^3 in U.S. units and g/L in metric units, where 1 kgr/ft^3 = 2.29 g/L.

Constituent	Concentration, mg/L $CaCO_3$	Concentration, gpg* $CaCO_3$
Calcium	194.0	11.35
Magnesium	70.2	4.11
Sodium	14.4	0.84
Potassium	1.5	0.09
Total hardness (TH)	264.2	15.45
Total cations (TC)	280.1	16.38
Bicarbonate	220.0	12.87
Chloride	5.2	0.30
Sulfate	54.0	3.16
Nitrate	0.9	0.05
Total anions (TA)	280.1	16.38
TMA	60.1	3.51
P alkalinity	—	—
M alkalinity	220	12.87
Carbon dioxide, as CO_2	11	0.64
Silica (reactive), as SiO_2	0.7	0.04

*Grains/gallon (1 lb = 7000 grains; 1 gpg = 17.1 mg/L)

Table 7.3 Raw Water Ionic Constituents Expressed in Common Ion Exchange Units

The amount of water that can be serviced by any given unit volume of resin is its capacity divided by ionic load. Equation (7.2) illustrates the relationship.

$$\text{Service water volume} = \frac{\text{exchange capacity}}{\text{ionic load}} \tag{7.2}$$

where Service water volume = volume that can be treated, gal (L)
Exchange capacity = resin ion exchange ability, gr as $CaCO_3$ (g as $CaCO_3$)
Ionic load = ion equivalents to be exchanged, gpg as $CaCO_3$ (g/L as $CaCO_3$)

In order to establish the amount of water that can be serviced by a particular vessel, the amount of resin in the vessel is incorporated into the equation as shown in Eq. (7.3).

$$\text{Service water volume} = \frac{\text{resin capacity} \times \text{resin volume}}{\text{ionic load}} \tag{7.3}$$

where Service water volume = volume that can be treated, gal (L)
Resin capacity = resin ion exchange ability, gr $CaCO_3/ft^3$ (g $CaCO_3$/L)
Resin volume = volume of active resin in vessel, ft^3 (L)
Ionic load = ion equivalents to be exchanged, gpg as $CaCO_3$ (g/L as $CaCO_3$)

While the above equation indicates optimum removal per vessel, the actual service run is usually lower due to kinetic and hydraulic inefficiencies.

Resin Regeneration

Ion exchange is a batch process. Once throughput capacity of the vessel is exhausted and undesirable ions start to leak into the outlet water flow, the unit must be taken off line and regenerated. This process reverses ion exchange that has been occurring in service and recharges resin back to the desired ionic form for service. Resin regeneration is usually accomplished in a co-current manner. The other method of regeneration is called counter-current. In the co-current regeneration process, there are four distinct phases (Fig. 7.7): backwash, regenerant addition, slow rinse, and fast rinse.

Backwash

Besides being a medium to exchange ions, resin is also a reasonably effective filter for suspended materials, which collect in the top section of the resin bed. Backwash is designed to expand the resin bed and remove accumulated suspended material. In addition, broken beads or resin fines migrate to the top of the bed during backwash, which removes them over time. Improper removal of this material

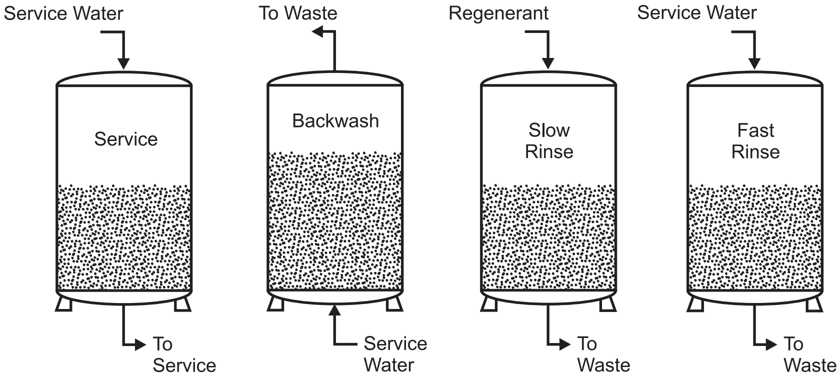


FIGURE 7.7 Four steps of co-current regeneration.

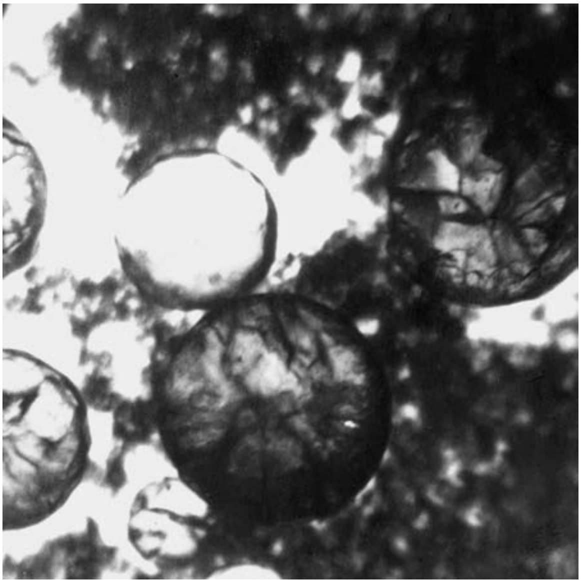


Figure 7.8 Gel-type resin containing a large amount of loose precipitate, indicating improper backwash. This condition is responsible for many problems with ion exchange equipment.

not only fouls the resin bed, but it also increases pressure drop values, putting more mechanical stress on the remaining beads (Fig. 7.8).

Flow and time are the two components that combine to make a good backwash. Flow must be adequate to fluidize the bed and expand it sufficiently to allow suspended material to be removed. Time allowed for backwash must be sufficient to allow removal of all suspended material. When backwash is complete, the bed is reclassified, and any channeling that formed during service is eliminated. Figure 7.9 shows a good backwash turbidity profile.

Backwashing involves reversing the normal service water flow through the vessel. Backwash water enters the vessel at the bottom and leaves the vessel at the top through the service water inlet. During backwash, the resin bed is expanded. A minimum expansion of about 50% is required for cation resins to ensure good suspended material removal and bed reclassification. Anion resins tend to require a little more bed expansion; 75% is a common recommendation for them.

Waters that are subject to seasonal variation in temperature experience density changes. At the same flow rate, colder, denser water has more lifting capability than warmer, less dense water. Plants with seasonal fluctuations in water temperature should adjust the backwash flow rate to avoid losing resin during times when cold water is

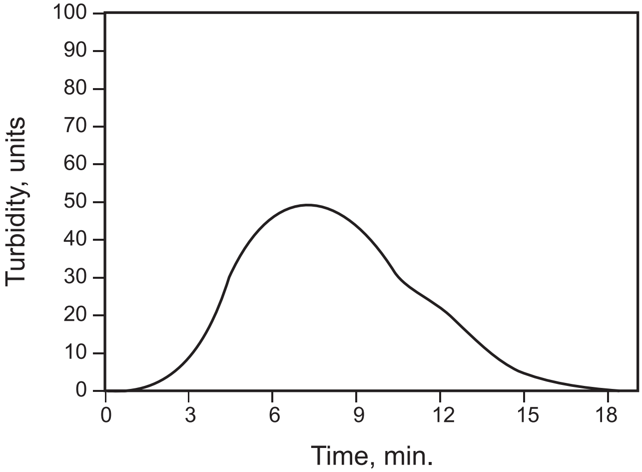


Figure 7.9 Turbidity profile of ion exchanger backwash.

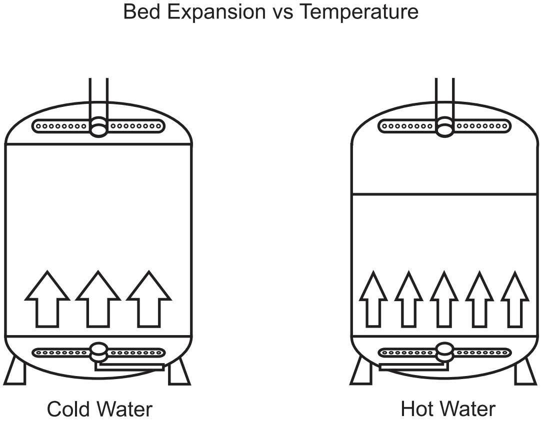


Figure 7.10 Bed expansion is governed not just by flow but also by water temperature.

in use, or getting insufficient solids removal when the water is warmer. Figure 7.10 illustrates the effect of water temperature on bed lift.

Regenerant Addition

Concentrated regenerant chemicals are typically diluted continuously in-line by being injected into a flow of dilution water of acceptable quality. Simple systems may employ a dilute chemical tank from which regenerant is pumped or educted and further diluted to the required concentration. The resulting plug of regenerant is moved through the resin bed, exchanging desired ions for undesired ones.

It is a basic principle of ion exchange that all of the water used for backwashing, regenerating, and rinsing resins should be the same as the normal inlet flow to that vessel. For regeneration of all systems employing anion exchange resins, regenerant dilution water must be cation unit outlet quality to prevent precipitation of hardness in resin and to maintain desired effluent quality.

During any regeneration, it is extremely important that the correct combination of regenerant concentration, flow rate, and contact time is maintained to achieve the required exchanger working capacity. Specific conductance meters, calibrated in percent regenerant concentration, can be used to monitor and alarm dilute regenerant concentrations.

Slow Rinse

The displacement (slow) rinse is very important and is actually part of the regenerant injection step. It is usually a continuation of the dilution water flow after regenerant addition is terminated. The displacement rinse clears the regenerant solution from the piping systems and pushes the regenerant plug remaining in the vessel slowly through the resin bed, continuing the regeneration step. This ensures that all regenerant is utilized by maintaining the required flow rate for efficient ion exchange.

The volume of water used should be more than one bed volume of resin. This may be greater with some design configurations in order to allow diffusion of regenerating ions through the interior of the resin beads to the surface, where they can be released into the slow rinse flow. Larger slow rinse volumes may reduce the required fast rinse volume and reduce total wastewater generation.

Fast Rinse

This step flushes remaining regenerant from voids or pockets in the resin bed and from resin particles themselves. This rinse is discharged to waste until it is free of excess chemical and undesirable ions. The fast rinse should be continued until reaching required effluent quality, keeping in mind that resin fouling or degradation may increase rinse volume requirements.

In-line analytical instrumentation, such as hardness and silica analyzers or conductivity monitors, can be used to indicate and alarm the endpoint of ion exchange regeneration or service.

Counter-Current Regeneration

In this method of regeneration, dilute regenerant flows in the opposite direction to the service flow. With downflow service, regeneration is upflow; with upflow service, regeneration is downflow. The heel of incompletely regenerated resin is at the service inlet end of the regenerated resin, and leakage is much lower than achievable with co-current regeneration (see Fig. 7.11).

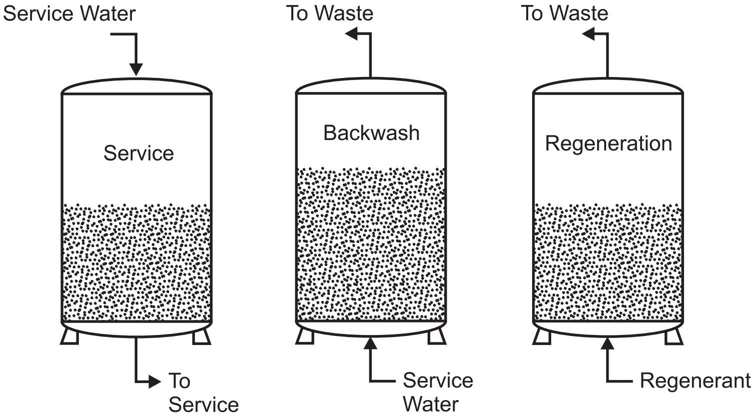


FIGURE 7.11 Counter-current regeneration. The backwash step only occurs periodically.

Counter-current regeneration performance is dependent on the resin bed being held in a compacted state, without it being allowed to fluidize. Fluidization allows resin to mix and results in the most completely exhausted beads populating the entire bed rather than remaining at the service inlet end of the bed. Fluidization is prevented by placing mechanical restrictions to movement, such as a regenerant collecting system buried in the resin bed approximately 6 inches (152 mm) from the service inlet end of the bed. This layer may be simply unregenerated working resin or inert beads. If the layer is working resin, it is not included in capacity calculations.

In addition, a blocking flow of water or compressed air is used in opposition to the regenerant flow to further prevent bed fluidization. Air block tends to dry and eventually break some resin particles, while water block increases the amount of wastewater generated.

These units are not backwashed with every regeneration but at intervals varying from every third to as little as every fortieth regeneration, depending on cleanliness of service water being treated. Once backwashed, resin must be regenerated at dosages double or triple normal levels to restore the service outlet end of the resin bed to a highly regenerated state. Failure to use increased dosage results in inability to produce the higher purity effluent expected.

Given all of these demands for successful counter-current regeneration it is not surprising that despite its benefits counter-current regeneration is used in only a small minority of ion exchange systems. Retrofitting or converting a conventionally regenerated system to counter-current operation is a considerable engineering project, and this should not be undertaken without a thorough understanding of the challenges that must be overcome.

Weakly functional resins such as weak acid cation and WBA derive little benefit from counter-current regeneration, and therefore, counter-current regeneration is rarely used in such units. Counter-current regeneration of strongly functional resins such as SAC and SBA offers a number of benefits:

- Dramatic reduction in ion leakage at lower regenerant dosage
- Increased regeneration efficiency
- Reduced chemical consumption
- Decreased waste treatment cost due to reduced regenerant waste

Resin Types

Modern synthetic ion exchange resins have different structures and functional groups. These differences allow the different resins to target different ions in water. Resins are categorized by function. Four basic types of resin used in water treatment are:

1. Strong acid cation (SAC)
2. Weak acid cation (WAC)
3. Strong base anion (SBA)
4. Weak base anion (WBA)

Strong Acid Cation

SAC resins operate across the entire pH range. Life expectancy of a quality SAC resin is 10 to 15 years, or even longer under ideal operating conditions. Life expectancy can be shortened due to a number of factors:

- Oxidation such as by free chlorine or chloramines
- Thermal shock
- Foulants such as iron, calcium sulfate, or aluminum as examples

SAC resins can remove all cations or just some cations, depending on regenerant used to recharge the resin. The amount of regenerant required for regeneration is considerably higher than stoichiometric levels. Common regenerant chemicals are sodium chloride (NaCl) and strong mineral acids such as sulfuric acid (H_2SO_4) and hydrochloric acid (HCl).

When a SAC unit is regenerated with NaCl, resin is put into the sodium form SAC (Na^+). In this form, resin exchanges sodium for the TH ions, mostly calcium and magnesium. When a SAC unit is regenerated with hydrogen from a strong acid such as H_2SO_4 or HCl, it is put into the hydrogen form SAC (H^+). In this form, resin exchanges for all cations.

Strong Acid Cation—Sodium Form

SAC (Na^+) softening is used in treatment of process water, boiler makeup, or any use involving removal of the scale forming ions, calcium and magnesium, and replacing them with completely soluble sodium ions. In the process, other cations with higher affinity for the resin than sodium are also removed. For instance, potassium is removed initially but is displaced from the resin as the ion exchange band containing hardness progresses down through the bed. This is the simplest ion exchange process, producing soft water, and is shown in Eq. (7.4) and Fig. 7.12.

$$Ca(HCO_3)_2 + 2RNa \xrightarrow{\text{flow}} R_2Ca + 2NaHCO_3 \tag{7.4}$$

As ion exchange is a batch process, resin continues to exchange sodium for calcium and magnesium until its capacity is exhausted. Regeneration is then required with a solution of sodium chloride brine at a concentration sufficiently high to overcome the inherent affinity of the resin for calcium and magnesium ions. The regeneration reaction is shown in Eq. (7.5).

$$2NaCl + R_2Ca \xrightarrow{\text{flow}} 2RNa + CaCl_2 \tag{7.5}$$

Reactions for magnesium are the same as Eqs. (7.4) and (7.5). Calcium ions have a stronger affinity for SAC resin than magnesium;

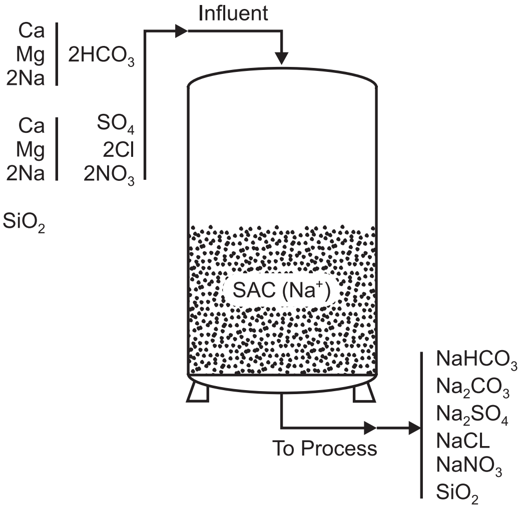


FIGURE 7.12 Typical SAC (Na^+) exchanger (sodium softener).

therefore, magnesium ions leak first at service break. These reactions are the same whether the softener is a primary unit, polishing unit, or installed after cold or hot lime softening systems.

Achievable working exchange capacities are dependent upon applied regeneration dosages and allowable hardness leakage. Working capacity is best determined from engineering data provided by resin manufacturers but can range from 20 to 30 kgr/ft^3 (46–69 g/L) of resin at 100% sodium chloride dosages ranging from 6 to 15 lb/ft^3 (96–240 kg/m^3) of resin. Working capacity and regenerant dosage should be selected to provide required service throughput between regenerations at reasonable regeneration efficiency and resin volume.

This process may be used in units or combinations of units employing:

- Co-current or counter-current regeneration
- Single unit or primary plus polishing unit train
- Normal or thoroughfare regeneration
- Conventional configuration for all applications or packed bed design (except following lime softening processes where packed beds should not be used)

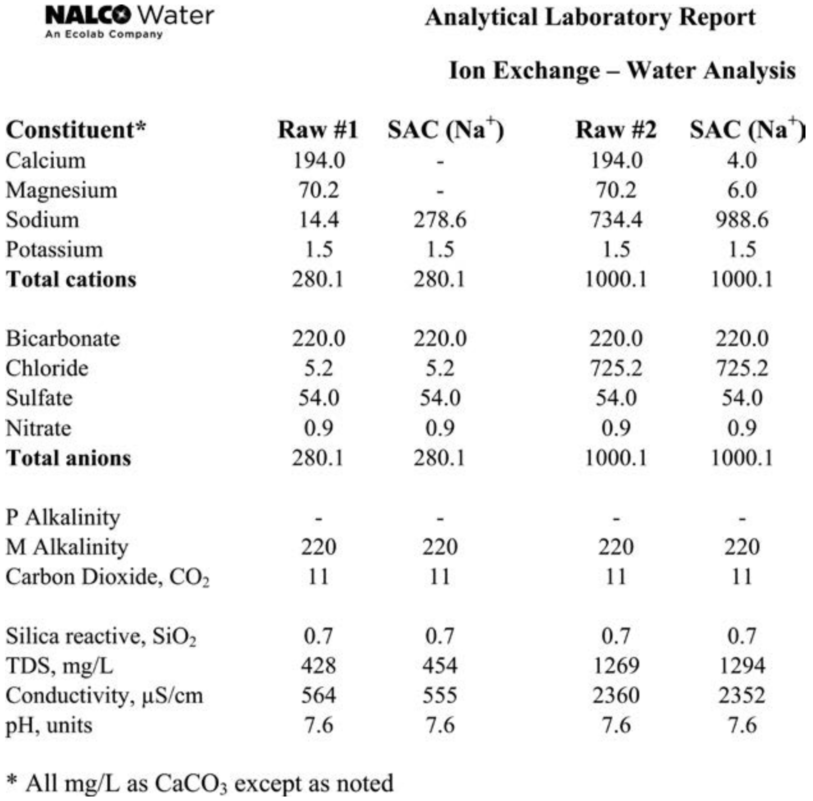
Regeneration conditions for flow rates, regenerant concentration, and contact time should be set as required for the particular application and dissolved solids concentration in the water to be treated. Hardness leakage increases as background total dissolved solids (TDS) concentration increases. Compensation requirements start when TDS exceeds 500 mg/L, and the degree of compensation is obtained from resin engineering data.

Figure 7.13 shows typical softening results using SAC (Na^+) for two different waters. Note the impact of the elevated sodium concentration in the second raw water.

Strong Acid Cation—Hydrogen Form

The SAC (H^+) process is one of the primary stages in demineralization, where it can be part of simple two-bed systems or more complex multiple-stage systems. It can be used as part of split stream dealkalization or as a single dealkalization process when combined with decarbonation.

The same resin used to remove hardness from water, when regenerated with sodium chloride, can be used to remove all cations from water, when regenerated to the hydrogen form with strong mineral acid. In acid form, the resin replaces all cations with hydrogen (H^+) ions. Chloride, sulfate, and nitrate are converted to corresponding strong mineral acids, while weakly ionized acids are created from bicarbonate and carbonate alkalinity and silica (see Fig. 7.14).



NALCO Water
An Ecolab Company

Analytical Laboratory Report

Ion Exchange – Water Analysis

Constituent*	Raw #1	SAC (Na^+)	Raw #2	SAC (Na^+)
Calcium	194.0	-	194.0	4.0
Magnesium	70.2	-	70.2	6.0
Sodium	14.4	278.6	734.4	988.6
Potassium	1.5	1.5	1.5	1.5
Total cations	280.1	280.1	1000.1	1000.1
Bicarbonate	220.0	220.0	220.0	220.0
Chloride	5.2	5.2	725.2	725.2
Sulfate	54.0	54.0	54.0	54.0
Nitrate	0.9	0.9	0.9	0.9
Total anions	280.1	280.1	1000.1	1000.1
P Alkalinity	-	-	-	-
M Alkalinity	220	220	220	220
Carbon Dioxide, CO_2	11	11	11	11
Silica reactive, SiO_2	0.7	0.7	0.7	0.7
TDS, mg/L	428	454	1269	1294
Conductivity, µS/cm	564	555	2360	2352
pH, units	7.6	7.6	7.6	7.6

* All mg/L as $CaCO_3$ except as noted

Figure 7.13 Illustrates effects of high TDS and sodium on softener performance. These analyses are based on co-current regeneration in conventional units. To achieve hardness leakage shown in right most SAC (Na^+) column, sodium chloride regeneration level must be increased 20%.

Typical chemical reactions for the exhaustion cycle are shown in Eqs. (7.6) to (7.8).

$$Ca(HCO_3)_2 + 2RH \xrightarrow{\text{flow}} R_2Ca + 2H_2CO_3 \tag{7.6}$$

$$MgCl_2 + 2RH \xrightarrow{\text{flow}} R_2Mg + 2HCl \tag{7.7}$$

$$Na_2SO_4 + 2RH \xrightarrow{\text{flow}} 2RNa + H_2SO_4 \tag{7.8}$$

Affinity of sodium for SAC (H^+) resin is lower than calcium and magnesium, and some sodium leakage always occurs. With effective counter-current regeneration, sodium leakage is less than 0.2 mg/L

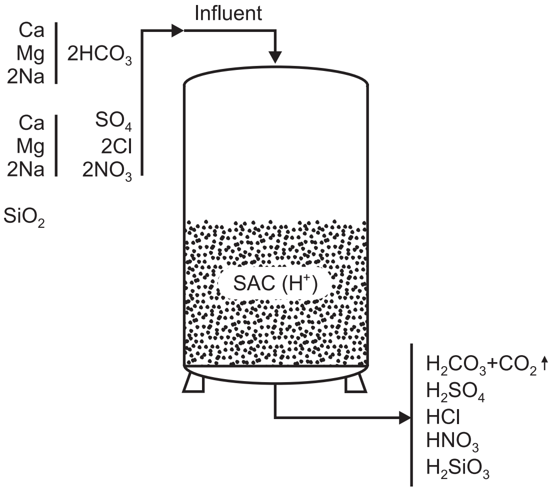


FIGURE 7.14 Typical SAC (H$^+$) exchange.

as $CaCO_3$. With co-current regeneration, the amount of sodium leakage is a function of:

- Ratio of sodium to TC—as percent sodium increases, sodium leakage increases.
- Ratio of alkalinity to TC—as percent alkalinity increases, sodium leakage decreases because less free mineral acidity (FMA) is created, decreasing the tendency to elute sodium ions. This is an important factor when SAC (H$^+$) resin is used for demineralization.
- Acid regeneration dosage—increasing acid dosage decreases sodium leakage.

However, when this process is used in co-current units for demineralizer applications, acid regeneration dosage is generally selected to ensure sodium leakage is less than 2 mg/L as $CaCO_3$. Increased sodium leakage presents as higher pH and conductivity values in the anion unit outlet stream. As with all ion exchange processes, the efficiency of regeneration and the amount and type of leakage are defined by the mechanical design of the internal distribution systems. Regeneration reactions are shown in Eqs. (7.9) to (7.11).

$$R_2Ca + H_2SO_4 \xrightarrow{\text{flow}} 2RH + CaSO_4 \tag{7.9}$$

$$2RNa + H_2SO_4 \xrightarrow{\text{flow}} 2RH + Na_2SO_4 \tag{7.10}$$

$$R_2Ca + 2HCl \xrightarrow{\text{flow}} 2RH + CaCl_2 \tag{7.11}$$

Equations (7.10) and (7.11) show formation of completely soluble salts, but Eq. (7.9) indicates the regeneration effluent contains calcium sulfate ($CaSO_4$) that has very low solubility in water and sulfuric acid. Its solubility is slightly better in hydrochloric acid, but even that must be heated to become truly effective in dissolving calcium sulfate.

SAC (H^+) units can be regenerated at higher concentrations of sulfuric acid; however, calcium sulfate precipitation remains a significant problem, requiring use of a stepwise regeneration technique that is not required when using hydrochloric acid for regeneration.

When regenerating SAC (H^+) resin with sulfuric acid, to avoid $CaSO_4$ precipitation, the initial dilute acid concentration used must be selected based on influent water ionic concentrations. In addition, dilute acid flow rate for injection must be sufficiently high to ensure acid containing eluted calcium is discharged from the resin bed before $CaSO_4$ crystals can develop.

Stepwise regeneration meets two objectives. The first step elutes most of the calcium from the resin at a concentration, in the dilute acid, less likely to precipitate $CaSO_4$ rapidly. The second step, at higher concentration, is necessary to achieve the degree of regeneration necessary in order to provide desired resin working capacity.

Some resin manufacturers recommend using as many as four dilute sulfuric acid concentrations, however, two or three steps tend to be the norm.This method requires that hydrogen ions be exchanged onto resin at ever-increasing exchange rates, which becomes more difficult as resin sites become more fully converted. It is preferredthat stepwise regeneration be confined to two steps and that concentration be changed by decreasing dilution water flow rate. This method provides a constant rate of hydrogen ion exchange to resin exchange sites.

The minimum dilute acid flow rate required for the first step in stepwise regeneration or for single-step regeneration can be calculated from Table 7.4.

% Ca of Total Cations as $CaCO_3$	Minimum Dilute Sulfuric Acid Flow Rate, gpm/ft³ (m³/[h·m³])
0	0.5 (4)
25	0.5 (4)
50	1.0 (8)
75	1.5 (12)
100	2.0 (16)

Table 7.4 Minimum Flow Rates for Sulfuric Acid Regeneration to Avoid $CaSO_4$ Fouling

When regenerating with dilute hydrochloric acid, there are no problems of precipitate formation, and dilute regenerant may be injected at 5% concentration by weight. Higher concentrations can lead to osmotic shock due to rapid change in resin volume. Dilute acid injection time should be at least 15 minutes with HCl.

Hydrochloric acid is a more efficient regenerant but is more expensive than sulfuric acid in North America. In addition, vessel internals cannot be constructed of stainless steel but must be of Hastelloy C or of nonmetallic construction.

Resin working capacity varies widely depending on influent water chemistry and regeneration level. With sulfuric acid, capacity may range from 8 to 25 kgr/ft^3 (18–57 g/L) at dosages of 3 to 10 lb/ft^3 (48–160 kg/m^3) of 66° Bé (93% H_2SO_4) acid. With hydrochloric acid, capacity may range from 12 to 33 kgr/ft^3 (27–76 g/L) at dosages of 6 to 30 lb/ft^3 (96–480 kg/m^3) of 30% HCl. Highest capacities are obtained on water with very high alkalinity and sodium concentrations.

Minimum resin bed depths should be 30 inches (0.76 m) in conventional co-current units and 5 ft (1.5 m) in counter-current units to allow for exchange reactions to be completed.

Weak Acid Cation

Weak acid cation (WAC) resins operate under alkaline conditions. These resins remove only hardness cations calcium and magnesium associated with alkalinity. WAC resin can be regenerated at stoichiometric dosages. Common regenerants are strong mineral acids such as sulfuric and hydrochloric or sodium chloride. When regenerated in the sodium form, resin is primarily used for hardness reduction of brackish water or polishing the effluent stream of lime softened water. Average life expectancy of WAC resin is the same as that of SAC, 10 to 15 years. This resin is subject to many of the same degradation issues as SAC, such as oxidation by free chlorine or chloramines and fouling from iron, calcium sulfate, or aluminum.

Weak Acid Cation—Hydrogen Form

A major advantage of the WAC (H^+) process is that it produces consistent effluent alkalinity regardless of variations in influent water. WAC (H^+) resin, having properties of weak carboxylic acid, is capable of exchanging cations of alkaline salts, but has no exchange capacity with neutral salts as illustrated in the following equations:

$$2RCOOH + Ca(HCO_3)_2 \xrightarrow{\text{flow}} (RCOO)_2Ca + 2CO_2 + 2H_2O \tag{7.12}$$

$$RCOOH + CaCl_2 \xrightarrow{\text{flow}} \text{no reaction} \tag{7.13}$$

Affinity of cations for this type of resin is typically

$$H^+ >> Cu^{+2} > Fe^{+2} > Ca^{+2} > Mg^{+2} > NH_4^+ > Na^+$$

From affinity data, it is apparent that

- Hydrogen has a very high affinity for WAC resin.
- Magnesium leaks in preference to calcium.
- Sodium associated with alkalinity reduces working capacity of WAC resins.

If TH exceeds alkalinity, hardness is reduced to exactly the same extent as alkalinity reduction when expressed as $CaCO_3$. When hardness is less than alkalinity, in addition to capacity reduction of the resin, it is important to realize that zero hardness is not achieved. Magnesium leaks at a concentration of 1 to 2 mg/L, and attempts to achieve zero hardness by artificially increasing alkalinity to exceed hardness have been unsuccessful.

Exhaustion chemical reactions are shown in Eqs. (7.14) and (7.15), and regeneration reactions are shown in Eqs. (7.16) and (7.17).

$$2RCOOH + Ca(HCO_3)_2 \xrightarrow{\text{flow}} (RCOO)_2Ca + 2H_2CO_3 \qquad (7.14)$$

$$2RCOOH + Mg(HCO_3)_2 \xrightarrow{\text{flow}} (RCOO)_2Mg + 2H_2CO_3 \qquad (7.15)$$

$$(RCOO)_2Ca + H_2SO_4 \xrightarrow{\text{flow}} 2RCOOH + CaSO_4 \qquad (7.16)$$

$$(RCOO)_2Ca + 2HCl \xrightarrow{\text{flow}} 2RCOOH + CaCl_2 \qquad (7.17)$$

As previously discussed, calcium sulfate has very low solubility in water and sulfuric acid, and only slightly higher solubility in cold hydrochloric acid. As a result, regeneration with sulfuric acid requires dilute acid (<0.8% by weight) to avoid precipitation of calcium sulfate in the resin bed and within resin beads. Use of hydrochloric acid eliminates the precipitation problem but imposes restrictions on materials of construction for internals. WAC (H^+) resin working capacity ranging from 30 to 38 kgr/ft^3 (69–87 g/L) is easily achieved while operating in starvation mode. Figure 7.15 is an example of a WAC exchanger in hydrogen form.

Two methods are used for acid regeneration of weak acid resins. In the United States, the most common method uses approximately 20% over the stoichiometric dosage of acid, which produces effluent containing FMA and pH less than 4.3 for a good portion of the service run. This requires pH adjustment after the decarbonator using sufficient caustic to neutralize FMA and residual CO_2. Acid regeneration level and caustic dosage are both higher than with the alternative starvation method discussed in the following section. In addition, residual TDS of the effluent is higher than achieved with the starvation method.

Achievable working capacity of WAC resins is affected by service water temperature. In very cold water, achievable working capacity is

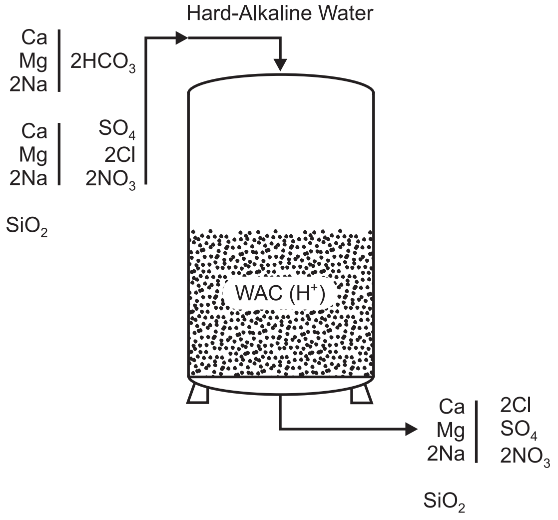


Figure 7.15 Weak acid cation in acid form.

reduced, and good design makes allowance for temperature variations. Automated starvation mode operation adjusts for such capacity changes as easily as it adjusts for alkalinity variations in influent water. A major advantage to starvation mode is that acid consumption is constant, virtually stoichiometric, even with varying water chemistry. The only changes would be in the service throughput per regeneration and the frequency of regenerations required for a unit.

Starvation Regeneration Method Outside of the United States, the most common method of regeneration uses only the stoichiometric acid dosage plus a minimal amount to neutralize alkalinity contained in acid dilution water. This method is referred to as starvation regeneration. With 110 mg/L M alkalinity in the water, using 0.8% by weight H_2SO_4 for regeneration at a resin rating of 36 kgr/ft^3 (82 g/L), the amount of excess acid required for starvation regeneration is about 2% above stoichiometric requirements.

With starvation regeneration, very little FMA is generated. This method is easily controlled and automated. Besides reducing acid consumed for the same treated water produced, caustic pH adjustment is required only to neutralize residual CO_2 from the decarbonator.

Acid injection is started at a constant service endpoint, for example, pH 5.8. Acid injection is terminated, either automatically or manually, when the effluent pH meter indicates a sudden drop in effluent pH. This occurs when the resin, which is very “hungry” for hydrogen ions, is fully regenerated, and acid breakthrough occurs. While a very small amount of FMA may be detected in the first few minutes of rinse, pH stabilizes with a small but positive alkalinity, typically from 2 to 5 mg/L as $CaCO_3$.

Automatic control of starvation regeneration simply involves shutting off the acid pump or acid ejector suction at acid breakthrough. The important objective is to terminate the service run at a constant pH and to control the volume of concentrated acid used for regeneration accurately.

Weak Acid Cation—Sodium Form

As mentioned earlier, WAC resin in sodium form is primarily used in treatment of brackish water or as a polisher for lime softening effluent. This ion exchange process of removing hardness ions from sodium chloride brine or brackish water solutions as concentrated as 2% by weight (20 000 mg/L) is shown in Eq. (7.18).

$$\mathrm{CaCl_2 + 2RCOONa \xrightarrow{flow} (RCOO)_2Ca + 2NaCl} \tag{7.18}$$

The reaction for magnesium is the same, but affinity for calcium is higher. WAC resin in sodium form is at its most swollen state, which is 60% larger than in acid form. During the exhaustion step shown in Eq. (7.18), the resin bed shrinks by 30% of its sodium form volume. Figure 7.16 shows a WAC exchanger in sodium form.

The resin continues to exchange sodium for calcium and magnesium until its capacity is exhausted. WAC resin cannot be regenerated from the exhausted state with sodium chloride or sodium hydroxide. However, WAC resin is readily converted to the sodium form if it is first regenerated to the acid (hydrogen) form. Regeneration is then

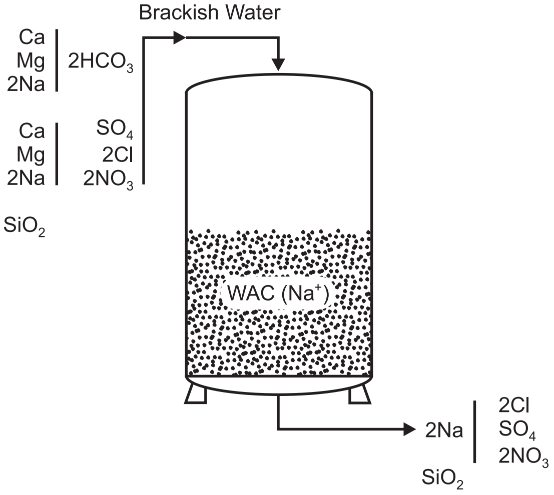


FIGURE 7.16 WAC exchanger in sodium form.

required, first with a solution of strong mineral acid, hydrochloric or sulfuric, at an acceptable concentration. The acid regeneration reaction is shown below using sulfuric acid as the regenerant.

$$(\mathrm{RCOO})_2\mathrm{Ca} + \mathrm{H_2SO_4} \xrightarrow{\text{flow}} 2\mathrm{RCOOH} + \mathrm{CaSO_4} \tag{7.19}$$

Following conversion to acid form, resin volume shrinks to approximately 35% of sodium form volume. The resin bed must now be regenerated to sodium form by a solution of sodium hydroxide. The caustic regeneration reaction is shown in Eq. (7.20).

$$\mathrm{RCOOH} + \mathrm{NaOH} \xrightarrow{\text{flow}} \mathrm{RCOONa} + \mathrm{H_2O} \tag{7.20}$$

Following completion of this step, WAC resin again swells to its maximum state and is 60% larger than in acid form. Since WAC resin regenerated into sodium form undergoes such major changes in volume, special consideration must be given to system and unit design. In order to withstand stress caused by repeated change in volume, stronger macroporous resins are used in preference to gel resins.

In theory, WAC resin can be regenerated at stoichiometric dosages for both acid and caustic regeneration. In practice, it has been found necessary to maintain a substantial excess to ensure satisfactory effluent hardness levels. Regeneration dosages are commonly 12.5 lb/ft^3 (200 kg/m^3) of both 100% HCl and 100% NaOH. Resin working capacities for hardness are typically about 40 kgr/ft^3 (92 g/L) for primary units and 17.5 kgr/ft^3 (40 g/L) for polishing units.

Strong Base Anion

SBA resins have three sub categories: Types I, II, and III. SBA resins remove all anions, including weakly ionized anions like carbon dioxide (CO_2) and silica (SiO_2). Regenerant dosages are considerably higher than stoichiometric.

Type I: Although resin manufacturer information suggests possible operation with water temperatures up to 140°F (60°C), these resins can be most safely operated and regenerated at temperatures of 122°F (50°C) and are used effectively on high alkalinity and high silica bearing waters. Common regenerants are sodium hydroxide (NaOH) and occasionally potassium hydroxide (KOH).

Type II: These resins have a lower temperature limit of 95°F (35°C), but they have higher working capacity than Type I resins. Type II resins are effective with high concentrations of carbon dioxide and silica. Common regenerants are sodium chloride (NaCl), sodium hydroxide (NaOH), and occasionally potassium hydroxide (KOH). Type II SBA resins are most often used in dealkalizer service.

Type III: This type of anion resin is less common. It exhibits the higher working capacity of Type II with the silica removal capacity and temperature limits of Type I. Common regenerants are sodium hydroxide (NaOH) and occasionally potassium hydroxide (KOH).

Strong Base Anion—Hydroxide Form

SBA (OH^-) units remove both strong mineral acids and weak acids produced by a SAC (H^+) exchanger, including carbonic and silicic acid (see Fig. 7.17).

The combination of SAC (H^+) and SBA (OH^-) resins in a demineralizer system, either in separate units or combined in a mixed bed demineralizer, is capable of producing effluent water with purity acceptable for use as feedwater in the highest pressure utility boilers. Provided proper upstream pretreatment is utilized, when combined in a mixed bed unit, the ion exchange process is capable of producing water having silica less than 0.01 mg/L and a specific conductance below 0.055 µS/cm or a resistance above 18.2 MΩ. This water purity is required for microchip manufacture. Equations (7.21) to (7.24) show SBA (OH^-) exhaustion reactions.

$$H_2SO_4 + 2ROH \xrightarrow{\text{flow}} R_2SO_4 + 2H_2O \tag{7.21}$$

$$HCl + ROH \xrightarrow{\text{flow}} RCl + H_2O \tag{7.22}$$

$$H_2SiO_3 + ROH \xrightarrow{\text{flow}} RHSiO_3 + H_2O \tag{7.23}$$

$$H_2CO_3 + ROH \xrightarrow{\text{flow}} RHCO_3 + H_2O \tag{7.24}$$

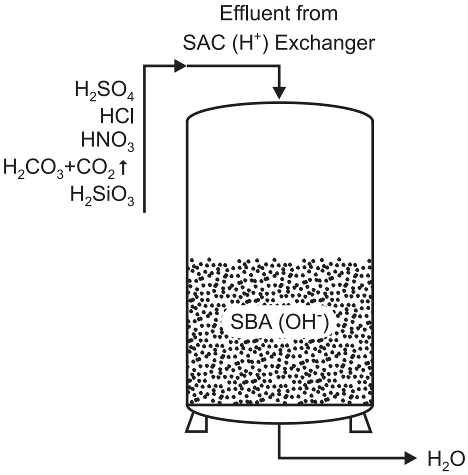


FIGURE 7.17 SBA exchanger in hydroxide form.

Regeneration must employ a strongly basic alkali such as caustic (NaOH).

$$R_2SO_4 + 2NaOH \xrightarrow{\text{flow}} 2ROH + Na_2SO_4 \qquad (7.25)$$

$$RCl + NaOH \xrightarrow{\text{flow}} ROH + NaCl \qquad (7.26)$$

$$RHSiO_3 + NaOH \xrightarrow{\text{flow}} ROH + NaHSiO_3 \qquad (7.27)$$

$$RHCO_3 + NaOH \xrightarrow{\text{flow}} ROH + NaHCO_3 \qquad (7.28)$$

Because strong base resin is highly ionized, caustic regenerant utilization is incomplete. As described earlier, Type I and Type II SBA have different regeneration efficiency, and excess regenerant dosages of 200 to 300% of the stoichiometric amount required to drive the reactions.

Depending on influent analysis and regenerant dosage, Type I resins typically provide a working capacity of 9 to 13 kgr/ft^3 (21–30 g/L), but these values can be improved considerably when the beads are regenerated with caustic at 120°F (49°C). Type II resins are expected to provide 16 to 21 kgr/ft^3 (37–48 g/L). Type III capacity falls between Type I and Type II. However, Type I resin is more chemically stable than Type II, and normal capacity loss is slower and less extensive. In addition, Type II resins are service water temperature sensitive, and silica leakage is slightly higher than with Type I resins.

To improve chemical efficiency of the demineralizing process, carbon dioxide formed by the SAC (H$^+$) unit is often removed with decarbonation or vacuum deaeration to reduce ionic load on the SBA (OH$^-$) resin and save caustic. This reduces both the resin volume and vessel size required. Mechanical, rather than chemical removal, usually becomes economical when carbon dioxide content exceeds 25% of the TEA load.

Because the SBA (OH$^-$) unit does not exchange cations, any cations leaking from the SAC (H$^+$) unit are present in anion effluent as alkalinity. Leakage through the SAC (H$^+$) unit is usually sodium, which the SBA (OH$^-$) converts to NaOH. Each mg/L of NaOH, expressed as $CaCO_3$, in the effluent creates a specific conductance of 5 μS/cm.

Strong Base Anion—Chloride Form

When silica removal is not a concern, SBA resin can be utilized in chloride form. In this form, SBA resin is particularly good for alkalinity removal. This is a two-stage process, with the primary treatment stage being SAC (Na$^+$) exchange. Anion influent must be completely softened water to ensure hardness is not precipitated in the anion resin (Fig. 7.18).

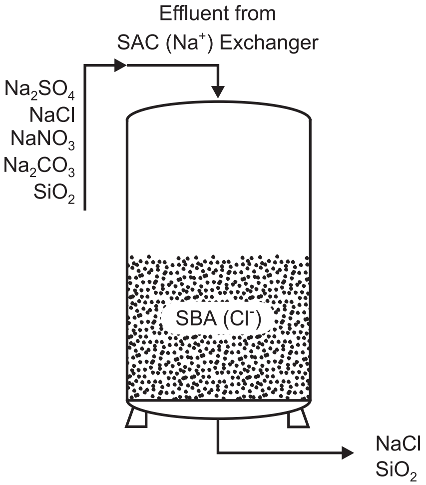


Figure 7.18 SBA exchanger in chloride form.

In addition, sodium chloride used for regeneration must be evaporated grade with very low hardness content, must be dissolved in soft water, and regenerant dilution water must be softened. Type II SBA resin is used to exchange chloride for bicarbonate, carbonate, nitrate, phosphate, and sulfate in the influent.

This process does not reduce TDS. In addition, the effluent is a very weak solution of sodium chloride. As a result, equipment such as unit piping and downstream service piping is likely to corrode and leak. Unit pipe work should be flanged and lined accordingly or be of all plastic construction where pipe size permits. In addition, ion exchange vessels should be lined on all surfaces contacted by the effluent and regenerant chemicals, and all internals should be corrosion resistant.

This process and its ion exchange kinetic characteristics differ considerably from other types of ion exchange, and the process cannot use the much higher cross-sectional flow rates applied to softening and demineralization systems. In addition, low working capacity of the resin usually dictates larger resin volumes to achieve acceptable service run times. Minimum resin bed depth is 3 ft (0.91 m), and the flow rate used is about 5 gpm/ft^2 [12 m^3/(h·m^2)].

Alkalinity leakage in the effluent is affected primarily by regenerant dosage, regenerants used, and characteristics of raw water, including TDS and chloride concentration.

Exhaustion chemical reactions are shown in Eqs. (7.29) and (7.30).

$$\mathrm{RCl} + \mathrm{NaHCO_3} \rightarrow \mathrm{RHCO_3} + \mathrm{NaCl} \tag{7.29}$$

$$\mathrm{2RCl} + \mathrm{Na_2SO_4} \rightarrow \mathrm{R_2SO_4} + \mathrm{2NaCl} \tag{7.30}$$

One regeneration reaction is shown in Eq. (7.31).

$$RHCO_3 + NaCl \xrightarrow{\text{flow}} RCl + NaHCO_3 \qquad (7.31)$$

Regeneration efficiency is quite low, particularly when sodium chloride is the sole regenerant. Resin working capacity ranges from 3.3 to 9.3 kgr/ft^3 (7.6–21 g/L) when regenerated at 4 lb/ft^3 (64 kg/m^3) of 100% sodium chloride. Regeneration efficiency ranges from a low of 10% to a high of 28% and is determined by TEA, ratio of M alkalinity to TEA, and concentration of chloride in the influent. Highest capacity is achieved with 90 to 100% M alkalinity:TEA and less than 10 mg/L chloride. Lowest capacity is achieved with less than 80% M alkalinity:TEA and 150 mg/L chloride. Obviously, application of this process is limited to low TDS waters due to economic considerations, as operating cost for regenerant chemicals is very high when compared to other alternatives.

If influent water has less than 100 mg/L chloride, resin working capacity of 10 kgr/ft^3 (23 g/L) can be achieved, if resin is regenerated with 4 lb/ft^3 (64 kg/m^3) of 100% sodium chloride plus 0.4 lb/ft^3 (6.4 kg/m^3) of 100% sodium hydroxide (caustic). This capacity is unaffected by the ratio of M alkalinity:TEA, but carbon dioxide must be included in the TEA calculation when caustic is used.

Effluent characteristics are quite different depending on whether or not caustic is used with sodium chloride (see Fig. 7.19).

The average life span of SBA resins is considerably shorter than that of SAC resins. SBA resins are not as durable and therefore require replacement sooner than corresponding SAC resin. Average life span for anion resins is 3 to 5 years for Type I and III and 2 to 3 years for Type II.

The most common foulant leading to reduced throughput capacity is high molecular weight organic molecules. These are not easily eluted from resin during regeneration, particularly if resin is in the chloride form. Hardness fouls anion resin, and silica is a common foulant in Type II resin. Thermal and osmotic shock play a role in capacity reduction, as does inferior quality regenerants. As SBA resin degrades, strong base sites are converted to weak base sites, which are not capable of exchanging for carbon dioxide or silica, and these tend to leak from the resin earlier.

Weak Base Anion

WBA resins exchange only strong mineral acids and have no capacity for carbon dioxide and silica. They can be regenerated at essentially stoichiometric dosages. Regenerants are sodium hydroxide (NaOH) and on occasion sodium carbonate (Na_2CO_3) or ammonium hydroxide (NH_4OH).

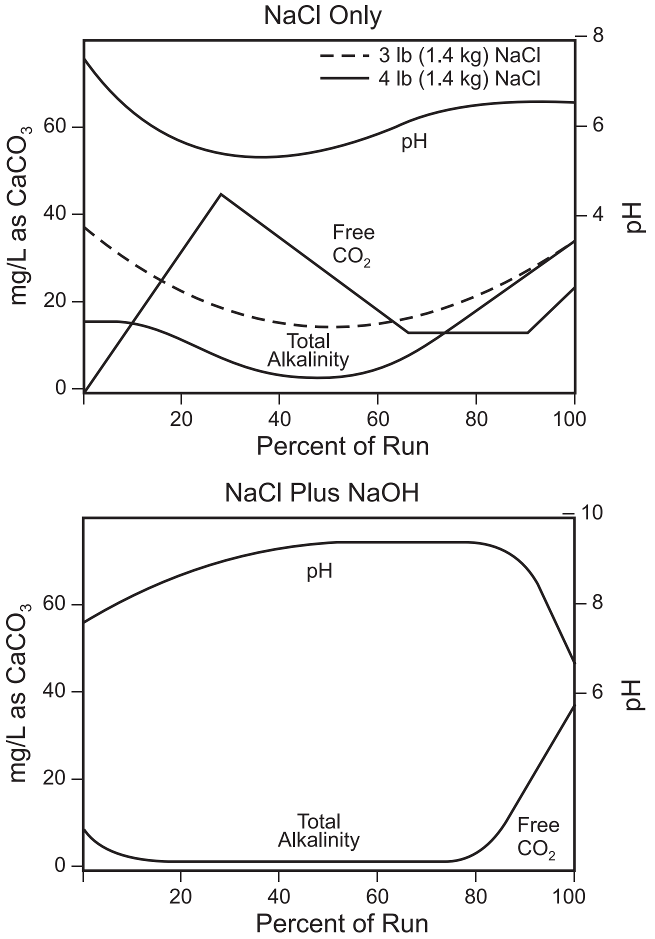


Figure 7.19 Dealkalizer performance with and without caustic addition.

Weak Base Anion—Hydroxide Form

A WBA (OH^-) unit removes only strong mineral acids produced by a SAC (H^+) exchanger, but not weak acids such as carbonic and silicic. Process applications such as mirror silvering, glass manufacture, metal plating, and automotive painting do not require removal of these weak acids. WBA (OH^-) resin is less costly to regenerate and much more efficient than SBA (OH^-). Because effluent still contains silica, effluent is not generally acceptable for boiler feedwater purposes (see Fig. 7.20).

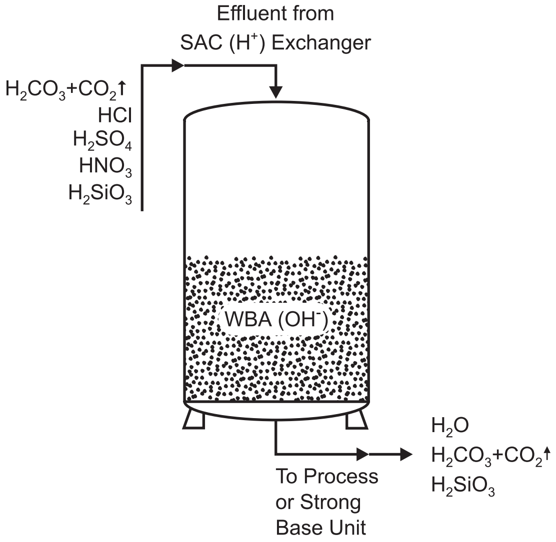


Figure 7.20 WBA exchanger in hydroxide form.

Reactions for removal of acids with WBA (OH^-) resin are illustrated below:

$$H_2SO_4 + 2ROH \xrightarrow{\text{flow}} R_2SO_4 + 2H_2O \tag{7.32}$$

$$HCl + ROH \xrightarrow{\text{flow}} RCl + H_2O \tag{7.33}$$

$$HNO_3 + ROH \xrightarrow{\text{flow}} RNO_3 + H_2O \tag{7.34}$$

As the weak base resin adsorbs the whole strong acid molecule, reactions are often shown simply as:

$$H_2SO_4 + 2R \rightarrow R_2H_2SO_4 \tag{7.35}$$

The common regenerant chemical used in WBA (OH^-) demineralization is caustic, but soda ash (Na_2CO_3) or ammonium hydroxide (NH_4OH) can be used. Reactions are shown in Eqs. (7.36) to (7.38).

$$R_2H_2SO_4 + 2NaOH \xrightarrow{\text{flow}} 2RNa_2SO_4 + 2H_2O \tag{7.36}$$

$$R_2H_2SO_4 + Na_2CO_3 \xrightarrow{\text{flow}} 2RNa_2SO_4 + H_2CO_3 \tag{7.37}$$

$$R_2H_2SO_4 + 2NH_4OH \xrightarrow{\text{flow}} 2R(NH_4)_2SO_4 + 2H_2O \tag{7.38}$$

Weak base ion exchange is a very efficient process requiring little more than the stoichiometric amount of regenerant, injected at a 4% as NaOH concentration, which neutralizes mineral acids attached to exchange sites.

When following a SAC (H^+) unit in a two-bed demineralizer system, the WBA (OH^-) unit produces effluent containing free carbon dioxide and silica. As a result, effluent pH is low, primarily due to carbon dioxide. It is usual to employ a decarbonator for mechanical removal of CO_2, but a decarbonator may be placed in two possible locations in a two-bed WBA (OH^-) demineralizer system.

If the decarbonator immediately follows the SAC (H^+) unit, residual carbon dioxide in WBA inlet is normally 5 to 10 mg/L depending on design. In that case, WBA (OH^-) effluent normally is about pH 6.5 to 8.0 for most of the service run. Specific conductance is greater than 20 μS/cm. With this arrangement, decarbonator transfer pumps must be designed to overcome anion unit pressure drop and have full service flow capacity plus anion rinse flow rate, which could equal the service flow rate.

Alternately, the decarbonator may be located immediately downstream of the WBA (OH^-) unit, which reduces pump discharge head and flow rate requirements. However, although WBA (OH^-) resins do not remove carbon dioxide, they do load carbon dioxide in the initial part of the service run and discharge it during the last part of the run. The decarbonator, therefore, must be designed to remove at least double the normal carbon dioxide concentration, which requires a larger unit.

Because the WBA (OH^-) unit does not exchange cations, any cations leaking through the SAC (H^+) unit are present in anion effluent. Leakage through SAC (H^+) is usually sodium, which WBA (OH^-) converts to NaCl. Each mg/L of NaCl, expressed as $CaCO_3$, in the effluent creates a nominal specific conductance of 2.5 μS/cm, but minimum specific conductance achieved is greater than 20 μS/cm from WBA (OH^-) units.

Weak base resins have very high working capacity, generally greater than 25 kgr/ft^3(57 g/L), but capacity is largely influenced by influent temperature and service flow rate. Working capacity may be 25% higher at 70°F (21°C) than at 40°F (4°C). Working capacity declines when service flow rates exceed 2 gpm/ft^3 (16 $m^3/[h \cdot m^3]$) of resin with a minimum bed depth of 3 ft (0.91 m).

Amines used in manufacturing weak base resins tend to degrade rapidly, which is manifested in development of long rinse times and high rinse water volume to obtain quality specifications following regeneration. Rinse water volume required with new resin can be more than 60 gal/ft^3 (8 m^3/m^3) of resin but might increase to 200 gal/ft^3 (27 m^3/m^3) in a relatively short time.

Average life span of WBA resin is 4 to 7 years. These resins are subject to degradation through thermal and osmotic shock, inferior regenerant quality, and hardness. WBA resin failure is generally seen as reduction of throughput capacity and longer rinse times.

Table 7.5 is a summary of ion exchange resins, regenerants used, and ions removed.

Resin Type	Form	Common Regenerants	Ions Removed
Strong acid cation (SAC)	Na^+	NaCl	Mg^{+2}, Ca^{+2}
Strong acid cation (SAC)	H^+	H_2SO_4, HCl	All cations
Weak acid cation (WAC)	H^+	H_2SO_4, HCl	Mg^{+2}, $Ca^{+2}$of alkalinity
Strong base anion (SBA) Type I	OH^-	NaOH, KOH	All anions
Strong base anion (SBA) Type II	OH^-	NaOH, KOH	All anions, limited on SiO_2 and CO_2
Strong base anion (SBA) Type II	Cl^-	NaCl	All anions, limited on SiO_2 and CO_2
Strong base anion (SBA) Type III	OH^-	NaOH, KOH	All anions
Weak base anion (WBA)	OH^-	NaOH, KOH	Strong mineral acids only
Weak base anion (WBA)	CO_3^{-2}	Na_2CO_3	Strong mineral acids only
Weak base anion (WBA)	NH_2^-	NH_3	Strong mineral acids only

Table 7.5 Resin Functionality by Regenerant

Resin Management

Many plants do not put into practice a good resin management program. As such, when resin failure occurs, it can be a shock to the maintenance budget. There are several key components in a resin management program. When taken together, they offer a clear picture of expected resin life, total operating cost, performance expectations, and cleaning cycles. Component pieces of a resin management program are: expected length of service, annual resin analysis, annual regeneration profile, monitoring service performance, chemical cleaning, and resin storage.

Expected Length of Service

Useful life of ion exchange materials is influenced by many factors:

- Influent water characteristics
- Operating environment such as service and regeneration conditions
- Resin chemical structure and stability
- Number of service/regeneration and cleaning cycles

- Exposure to oxidants and foulants
- Thermal and osmotic shock
- Attrition

Influent Water Characteristics

Influent water may contain natural substances or other materials from pretreatment processes or as the result of inefficient pretreatment. This can include suspended matter, turbidity, incompletely reacted precipitation chemicals such as lime, heavy metals such as iron and aluminum, excess polymers, system corrosion products, naturally occurring organics, and contaminants from plant process leaks. Any of these can cause fouling of resin-exchange sites, reducing effectiveness and leading to premature failure.

Operating Environment

Wide and sudden variations in influent water temperature may cause thermal shock and have an impact on useful resin life. This can include backwash water and regenerant solutions. Osmotic shock can occur from inaccurate control of regenerant concentration, leading to rapid changes in resin bead size from one form to another. Quality of regenerant dilution water is a factor in resin life, as internal and external fouling precipitates can be formed.

Resin Chemical Structure and Stability

Ignoring the effects of foulants, oxidants, etc., cation resins are more stable than anion resins, and life expectancy of cation resins is greater than that of anion resins. Type I SBA resins are more stable than Type II, again ignoring effects of fouling, etc. Amines used in anion resin manufacture have finite life spans. As amines degrade, resin loses strong base functionality (salt splitting capacity) and the ability to remove silica and carbon dioxide.

Number of Service/Regeneration and Cleaning Cycles

Each time a resin is exhausted, regenerated, or chemically cleaned, bead size and volume change. This can cause weak beads to crack or break, making them more likely to be washed from the unit during backwash. Bead breakage is called attrition.

Anion resin amine degradation occurs to some degree every regeneration. This results in gradual reduction in total capacity. Regeneration occurs more frequently as influent water TDS increases.

Effects of Oxidants

Residuals of oxidants such as chlorine and chloramines added to water for microorganism control attack the resin skeleton of cation resins. The divinylbenzene crosslink is permanently destroyed, and resin loses total capacity, takes on more water, and expands (Fig. 7.21). This increased bed pressure drop accelerates bead damage, and

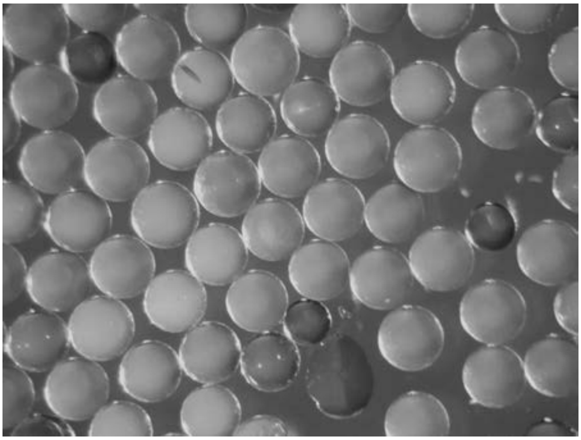


Figure 7.21 This cation resin has suffered oxidation and the reduction of divinylbenzene crosslinkage. The current moisture content of this resin is significantly higher than recommended.

degraded resin, being less dense, is lost to waste discharge during backwash. Results can be reduced service throughput, inability to meet effluent quality requirements (high leakage), increased regeneration frequency, increased resin replacement frequency, long rinses, increased waste generation, and high operating costs.

Oxygen is released in water by heating, either for energy conservation, system operating requirements, or more efficient regeneration of resins. Oxygen attacks both cation and anion resins, causing the same effects noted earlier.

Exposure to Foulants

Fouling may be reversible or irreversible, depending on the nature of the foulant and resin. Cation resins, usually being in a primary position in a system, are potentially exposed to suspended matter, turbidity, precipitated compounds from pretreatment, heavy metals, hydrocarbons, microorganisms, etc. In addition, heavy metal concentration and contaminants in regenerant acid may be present due to contaminated shipping containers, bulk trucks or corrosion of storage and handling equipment.

Anion resins are potentially exposed to organic acids, microorganisms of different types, and heavy metals from regenerant chemicals, etc. In addition, degradation products from cation resin oxidation cause irreversible fouling of SBA (OH^-) resins.

All of these foulants can form a film around a resin bead or block surface and internal exchange sites (Fig. 7.22). This impedes ion exchange reactions in both service and regeneration. Results can be

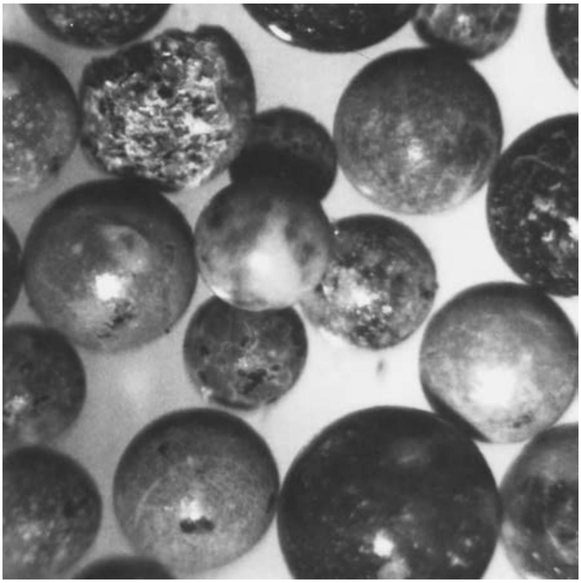


Figure 7.22 External organic and inorganic fouling of gel-type resin.

reduced service throughput, inability to meet effluent quality requirements (high leakage), increased regeneration frequency, increased cleaning and resin replacement frequency, long rinses, increased waste generation, and high operating costs.

The most common foulant in cation resins is iron, which is normally found in well water as ferrous iron (Fe^{+2}). Ferrous iron exchanges onto resin but is converted to ferric iron (Fe^{+3}) as oxygen in service and backwash water reacts with ferrous iron. Resin holds onto trivalent iron very strongly, which is not eluted completely. Further oxidation forms insoluble iron oxides that foul resin internally and externally. Proper diffusion is prevented, and unit effluent quality decreases while rinse volumes increase. Iron may be introduced to cation resin via contaminated acid or as a result of corrosion of the acid storage and handling system.

Iron is frequently found on anion resin and is the result of contaminated caustic or corrosion of the caustic storage and handling equipment. Iron in influent water reacts with organics that foul anion resin, leading to iron fouling of anion resin.

Aluminum is another common cation resin foulant. It can originate in raw water but more commonly results from overfeed of aluminum sulfate (alum) at the raw water treatment plant. It is very difficult to remove from resin because of its trivalent state.

Table 7.6 summarizes common resin foulants.

Resin Type	Common Foulants
SAC, WAC	Iron (oxidizes on surface and in resin pores) Aluminum Inorganic precipitates Cationic polyelectrolytes Microbiological growths
SBA, WBA	High molecular weight organic acids Iron hydroxide Anionic polyelectrolytes Cation resin degradation products Microbiological growths

TABLE 7.6 Typical Foulants Found on Ion Exchange Resins

Thermal Shock

This occurs with sudden temperature change in water entering a unit, such as in SAC (Na^+) hot water operations following hot lime softening or in condensate polishing. If cold water is introduced suddenly for backwashing or regenerating, resin can crack or shatter. To eliminate this problem, the rate of temperature change must be minimized by introducing cold water at a low-flow rate until resin is cooled sufficiently.

Osmotic Shock

Osmotic shock occurs in resin due to sudden changes in resin bead size or volume. This can be induced by rapid change in solution concentration in contact with resin. For instance, acid regeneration of WAC resin immediately followed by regeneration with caustic can cause this shock, as the increase in resin volume may be 60%. Additionally, osmotic shock may be caused in exhausted resin when contacted by overly concentrated acids or bases.

Attrition

Attrition, or physical breakage, occurs when resin beds are severely compacted by being in service for extended periods without backwashing. Accumulation of dirt or suspended matter increases bed differential pressure and contributes to breakage.

When resin beads break, smaller particles increase differential pressure and can cause further breakage. Similarly, very fine resin particles cause the same condition (Fig. 7.23).

Effects of osmotic shock and attrition include:

- Particle fragmentation
- Resin loss during backwash
- Increased bed pressure differential

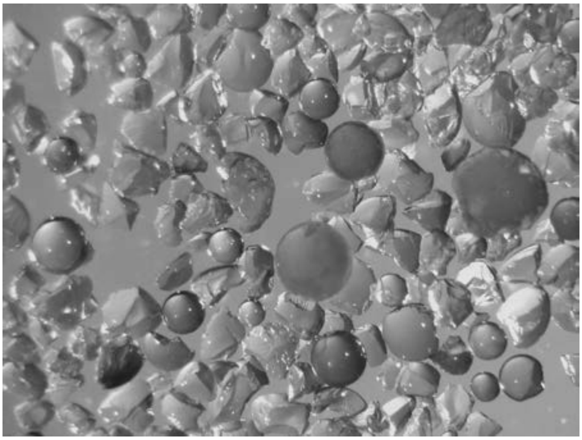


Figure 7.23 Badly cracked gel-type resin, which may be caused by internal precipitate or osmotic shock, the latter being common in hot lime softening units if pressure is suddenly released.

- Channeling of service and regenerant flows
- Reduced service throughput
- High ionic leakage (slippage)

Annual Resin Analysis

Effects of stresses on resin as mentioned earlier are measured by specific analytical tests, which should be conducted on core resin samples taken from every unit annually. Results should be compared to characteristics of a retained sample of new resin tested at the same time as the first used resin sample is tested.

Proper sampling of resin in an ion exchange unit for analysis is of paramount importance, since results of analysis should lead to positive recommendations for cleaning or replacing resin. The best time to take a sample of resin is after normal regeneration. This is especially important if levels of contaminants are required.

Avoid taking a resin sample scraped quickly from the top of the bed, because resin condition at the top is irrelevant of resin condition of the bed in general (Fig. 7.24). Instead, obtain a core sample of resin, preferably several core samples from each quadrant as seen in Fig. 7.25. These samples are then combined into one container for a composite analysis of the resin bed. Common tests used for resin evaluation include: water retention capacity (WRC), total capacity wet (TCW), salt splitting capacity (SSC), microscopic analysis, metals content, and physical condition.

Contaminant levels considered small, moderate, or high should be provided for guidance. The cause of any contaminant found and

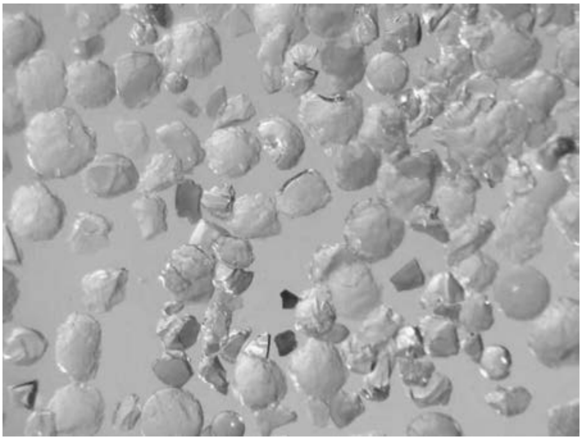


Figure 7.24 Picture of a resin sample scraped from the top of the bed. The sample is not at all representative of the core and exhibits mostly broken beads.

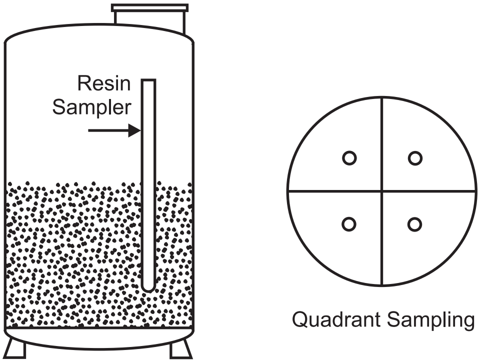
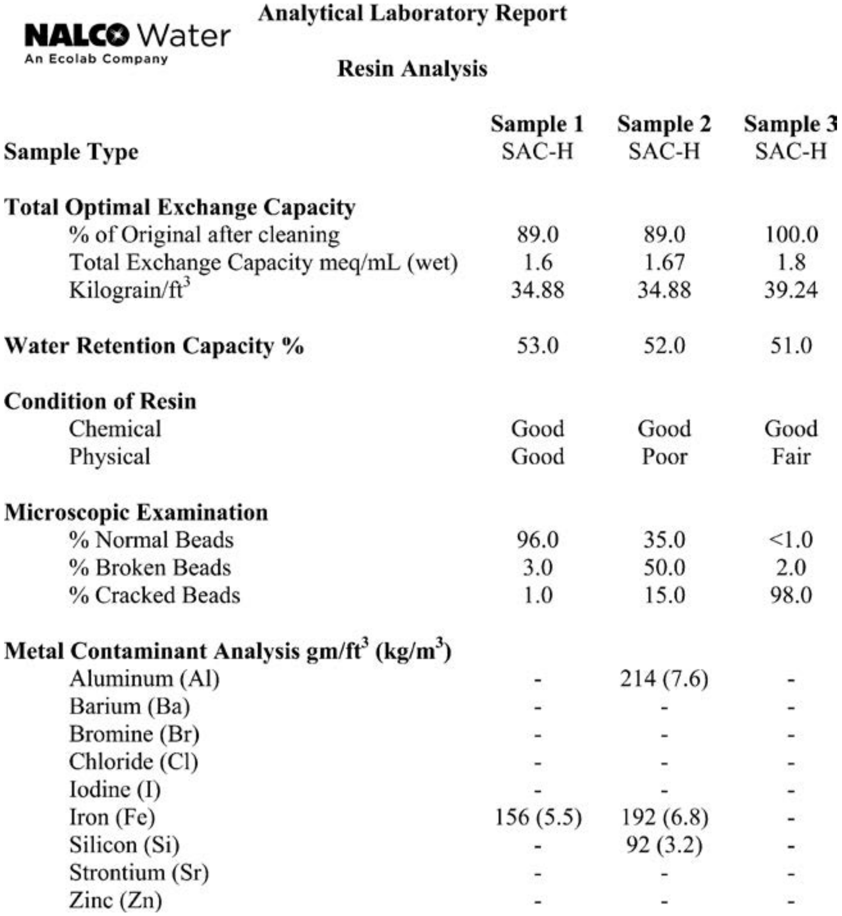


Figure 7.25 Obtaining resin core samples.

reported as high should be investigated and eliminated. Chemical cleaning for removal should be evaluated, taking into account length of service time on the resin. High iron on a resin in service for ten years may not be as significant as the same iron level on a resin that has been in service for only six months.

Figures 7.26 to 7.29 are typical resin analysis examples for SAC resins with the accompanying photographs. Sample 1 indicates that the resin in is good condition both physically and chemically. There is however, a large amount of iron fouling in the resin and inhibiting the exchange capacity. The iron in this case is both on and inside the resin bead. Sample 2 indicates a resin in good condition chemically but in



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Analytical Laboratory Report

Resin Analysis

	Sample 1	Sample 2	Sample 3
Sample Type	SAC-H	SAC-H	SAC-H
Total Optimal Exchange Capacity			
% of Original after cleaning	89.0	89.0	100.0
Total Exchange Capacity meq/mL (wet)	1.6	1.67	1.8
Kilograin/ft^3	34.88	34.88	39.24
Water Retention Capacity %	53.0	52.0	51.0
Condition of Resin			
Chemical	Good	Good	Good
Physical	Good	Poor	Fair
Microscopic Examination			
% Normal Beads	96.0	35.0	<1.0
% Broken Beads	3.0	50.0	2.0
% Cracked Beads	1.0	15.0	98.0
Metal Contaminant Analysis gm/ft^3 (kg/m^3)			
Aluminum (Al)	-	214 (7.6)	-
Barium (Ba)	-	-	-
Bromine (Br)	-	-	-
Chloride (Cl)	-	-	-
Iodine (I)	-	-	-
Iron (Fe)	156 (5.5)	192 (6.8)	-
Silicon (Si)	-	92 (3.2)	-
Strontium (Sr)	-	-	-
Zinc (Zn)	-	-	-

Figure 7.26 Typical SAC resin analyses.

poor condition physically. The exchange capacities are similar to sample 1 but physically the beads have suffered significantly. There is also a significant amount of contaminant on the beads in the form of aluminum and iron that will inhibit ion exchange. Sample 3 indicates a resin that has suffered extreme physical stress. Across all of the samples you can see that even though the beads are in various states of physical decline, chemically they are still functioning reasonably well. This is common with cation resin. They often fail physically prior to failing chemically.

Figures 7.30 to 7.33 are typical resin analysis examples for SBA resins with the accompanying photographs. Sample 1 reveals a resin that still has reasonable salt splitting capacity but is experiencing

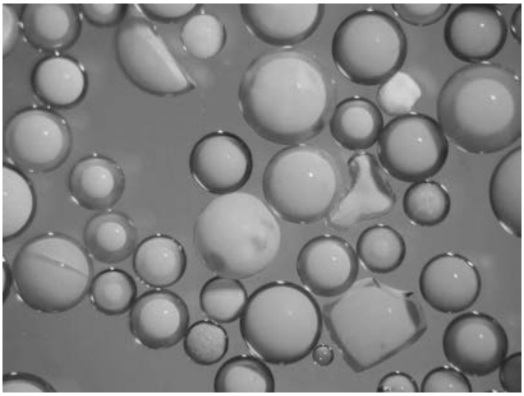


Figure 7.27 Sample resin #1 showing significant iron fouling both inside and on the resin bead.

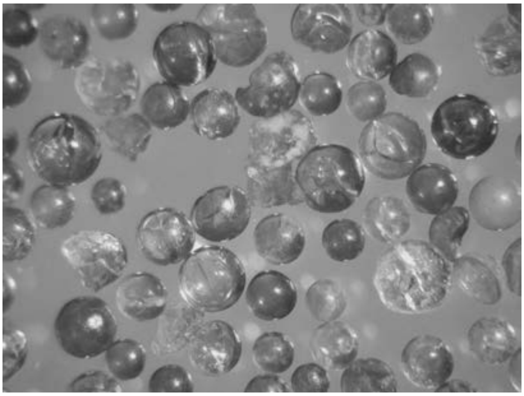


Figure 7.28 Sample resin #2 showing stressed beads with iron and aluminum fouling.

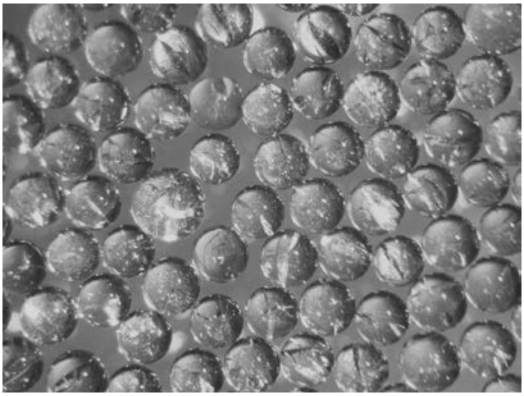
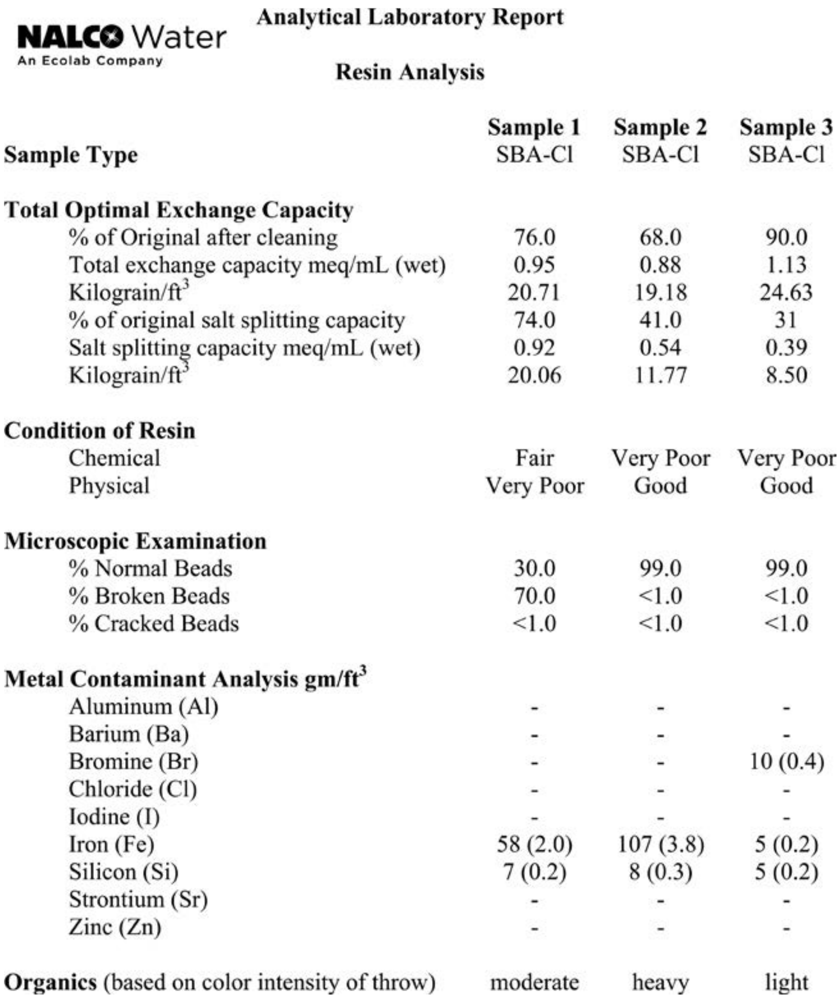


Figure 7.29 Sample resin #3 showing extremely stressed beads.



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Resin Analysis

Sample Type	**Sample 1** SBA-Cl	**Sample 2** SBA-Cl	**Sample 3** SBA-Cl
Total Optimal Exchange Capacity			
% of Original after cleaning	76.0	68.0	90.0
Total exchange capacity meq/mL (wet)	0.95	0.88	1.13
Kilograin/ft^3	20.71	19.18	24.63
% of original salt splitting capacity	74.0	41.0	31
Salt splitting capacity meq/mL (wet)	0.92	0.54	0.39
Kilograin/ft^3	20.06	11.77	8.50
Condition of Resin			
Chemical	Fair	Very Poor	Very Poor
Physical	Very Poor	Good	Good
Microscopic Examination			
% Normal Beads	30.0	99.0	99.0
% Broken Beads	70.0	<1.0	<1.0
% Cracked Beads	<1.0	<1.0	<1.0
Metal Contaminant Analysis gm/ft^3			
Aluminum (Al)	-	-	-
Barium (Ba)	-	-	-
Bromine (Br)	-	-	10 (0.4)
Chloride (Cl)	-	-	-
Iodine (I)	-	-	-
Iron (Fe)	58 (2.0)	107 (3.8)	5 (0.2)
Silicon (Si)	7 (0.2)	8 (0.3)	5 (0.2)
Strontium (Sr)	-	-	-
Zinc (Zn)	-	-	-
Organics (based on color intensity of throw)	moderate	heavy	light

Figure 7.30 Various typical SBA resin analyses illustrating different states of deterioration.

moderate organic fouling and significant physical stress as seen with the high amount of broken beads. Sample 2 shows a resin with a high level of organic fouling and a low salt splitting capacity. Sample 3 is of a resin that has light organic fouling but has lost a very significant amount of salt splitting capacity. As is typical of anion resins, they often loose salt splitting ability before they fail physically. All of these resins are candidates for replacement.

Prediction of Remaining Resin Life

Determining when resin is sufficiently degraded to warrant replacement is a difficult and somewhat complicated process. To a large

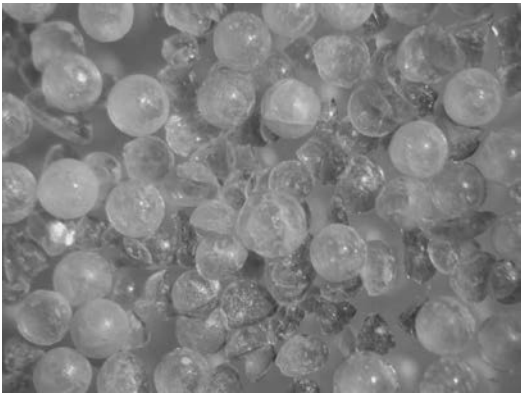


Figure 7.31 Sample resin #1 exhibits a moderate fouling with organics with a high percentage of broken beads.

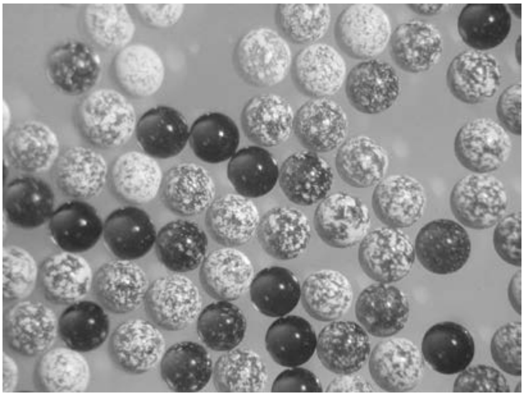


Figure 7.32 Sample resin #2 is heavily fouled with organics. Physically the resin looks to be in good condition but it has lost almost 60% of its salt splitting capacity.

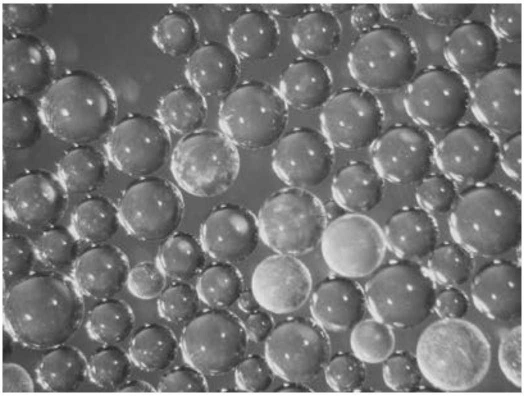


Figure 7.33 Sample resin #3. Physically the resin looks to be in good condition but it has lost almost 70% of its salt splitting capacity.

degree, the decision to replace is based on cost of replacement resin compared to increased labor and regenerant chemical costs resulting from shorter service runs and more frequent regenerations. In addition, degraded resins may cause higher ionic leakage and poor quality water. No hard and fast rules can be stated, and each case must be determined individually based on plant conditions.

Generally, SAC resins can have a substantial service life, provided there is no physical bead breakdown due to conditions outlined earlier. Normal attrition can be expected to be less than 3% per year. However, attack by oxidants causes increased water retention as bead cross-linking is attacked and beads swell. This is detected by the water retention capacity test, and results can be used as a rough rule-of-thumb to predict remaining resin life. Figure 7.34 is only applicable to standard gel-type SAC resins that have an average water retention capacity of 46 to 56% when tested in the hydrogen form.

SBA resins, on the other hand, experience continuous and gradual loss of total capacity because of the relatively less stable composition of the active exchange sites. As this normal degradation proceeds, SBA resins lose ability to exchange weak silicic and carbonic acid anions, while retaining ability to exchange strong anions (sulfate, chloride, and nitrate). This is detected by a decrease in salt splitting capacity (development of weak base sites from strong base sites). Under ideal service conditions, Type I resin life is typically less than five years, while Type II resin life is less than three to four years.

In new strong base anion resins, salt splitting capacity should be 100% of total exchange capacity. This determination can be used as a rough rule-of-thumb to predict remaining resin life. Figure 7.35 is only applicable to standard gel-type SBA resins.

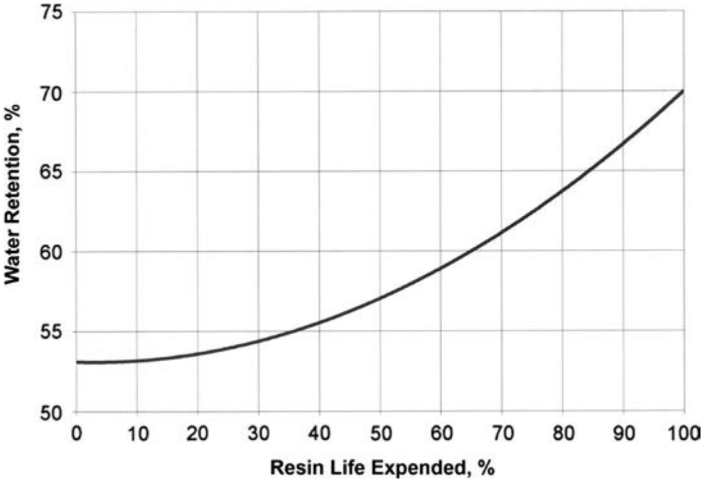


Figure 7.34 Useful life expended for SAC resin.

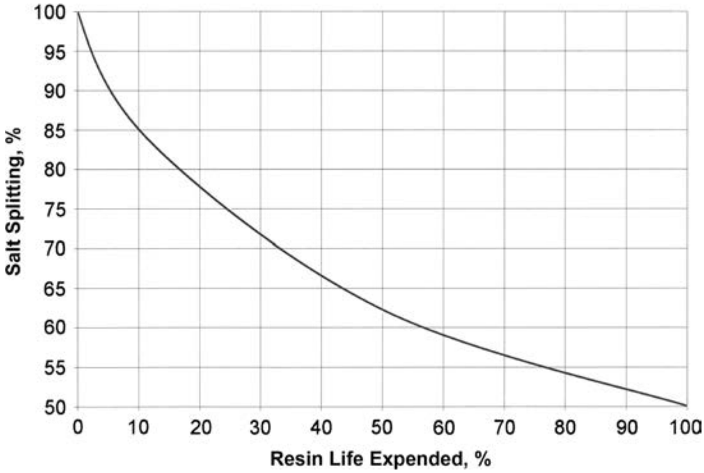


Figure 7.35 Useful life expended for SBA resin.

Annual Regeneration Profile

An annual elution study is of particular benefit to SAC (Na^+) and SBA (Cl^-) units. Since both units are regenerated with sodium chloride, an elution study using a salometer to evaluate a set of timed samples provides insight into brine saturation level as well as salt contact time. Adjusting brine intake or rinse flow rates, to manage the salt saturation curve, to that recommended for the resin, helps ensure good quality effluent. Figure 7.36 shows a proper brine plug moving through a SAC (NA^+) bed.

While an elution study is generally of most benefit to a sodium chloride regenerated resin, this method can be used on any co-current regenerated vessel with any regenerant. This is of most benefit when looking for early regenerant breakthrough due to channeling. Otherwise, comparing performance of a unit against original specifications for items noted below yields information necessary for regeneration or service adjustments.

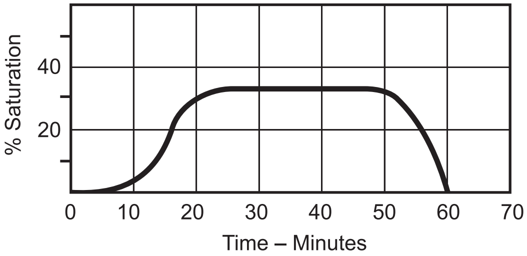


Figure 7.36 Ideal SAC (Na^+) elution curve.

- In service cross-sectional and volumetric flow rates
- Regeneration cross-sectional volumetric flow rates
- Comparison of actual service run length to specification
- Regenerant usage per volume of resin
- Regeneration water temperatures
- Backwash turbidity study
- Seasonal water temperature variation

Monitoring Service Performance

Monitoring ion exchange equipment effluent while in service is a task that is done regularly. Breakthrough or leakage of undesirable ions into service water gives an indication of when action needs to be taken and the unit regenerated.

SAC (Na^+)

SAC (Na^+) service performance and service endpoint are usually monitored by simple total hardness tests available to most operators. Alternately, online hardness analyzers may be used but are expensive. Figure 7.37 shows the breakthrough profile for a SAC (Na^+) unit.

SAC (H^+)

SAC (H^+) service performance and service endpoint are not easily monitored by simple chemical tests available to most operators. The only parameters that can be tested dependably are effluent FMA and

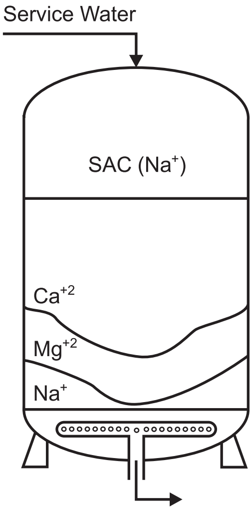


Figure 7.37 Breakthrough profile for SAC (Na^+) unit.

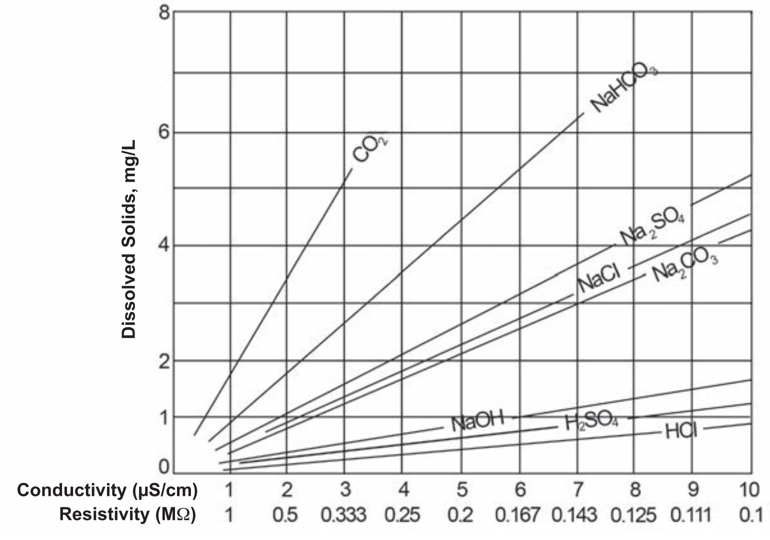


Figure 7.38 Conductivity (resistivity) of ionic species to dissolved solids.

sodium leakage. Total hardness can be monitored but should not be present at high concentrations (<0.2–0.5 mg/L as $CaCO_3$), unless the unit is grossly over exhausted or $CaSO_4$ precipitation has occurred. When SAC (H^+) resin begins to exhaust, there is a decrease in effluent FMA with a corresponding increase in sodium leakage. Decreasing FMA can be detected by a decrease in specific conductance of the effluent. However, as this measurement varies considerably with changing sulfate, chloride, and nitrate concentrations in inlet cation water, it is sometimes difficult to monitor accurately. In addition, the change can be very small and difficult to detect being only about 5 µS/cm per mg/L change from H_2SO_4 to Na_2SO_4 (Fig. 7.38). The usual method employed is comparison of FMA titrations or specific conductance values with those of companion cation units still in service producing satisfactory effluent.

Sodium analysis with online analyzers is quite accurate, but such analyzers are expensive and not utilized extensively, except at power generation plants where high-pressure boilers are in use.

Exhaustion may also be checked by measurement of SAC (H^+) outlet pH as compared to companion cation units. The pH rises with a drop in effluent FMA, but the change is quite small and difficult to measure accurately.

As SAC (H^+) sodium leakage increases, sodium ions from the SAC (H^+) combine with an equivalent number of hydroxide ions to form caustic (NaOH) in the anion effluent. Each mg/L of NaOH (expressed as $CaCO_3$) in the SBA (OH^-) effluent results in a specific

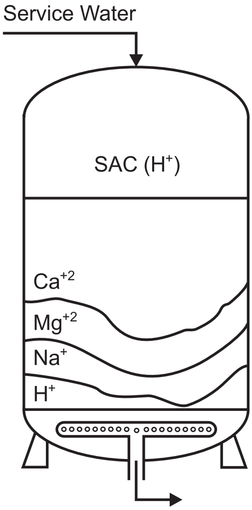


Figure 7.39 Breakthrough profile for SAC (H^+) unit.

conductance of 5 µS/cm. Therefore, an increase in sodium leakage of 1 mg/L causes an increase in SBA (OH^-) specific conductance of 5 µS/cm due entirely to cation performance. This can occur if SAC (H^+) and SBA (OH^-) service capacities are mismatched or if resin loss or degradation occurs in one or the other. The SAC (H^+) unit should be suspected first as the cause of service break, unless the system is anion capacity limited. Additionally, silica leakage from SBA (OH^-) increases with rising sodium leakage from the SAC (H^+). Figure 7.39 shows the breakthrough profile for a SAC (H^+) unit.

SBA (OH^-)

SBA (OH^-) units are usually monitored using effluent silica and specific conductance analyses. Both parameters are easily tested by operators but are frequently monitored continuously with online analyzers.

Silica, having lower affinity for SBA resin than other anions, leaks first. Silica does not contribute to effluent conductivity and is not detected by specific conductance instrumentation. Silica break may occur at 85 to 95% of the service run as opposed to specific conductance break at 100%.

pH measurements are not usually recommended as reliable service monitors for demineralizers but can be useful in determining whether the SAC (H^+) or SBA (OH^-) unit is responsible for service break. pH is observed simply and even litmus paper can be used, if a portable pH instrument is unavailable. Figure 7.40 indicates how the exhausted unit may be identified using pH, specific conductance, and silica determinations.

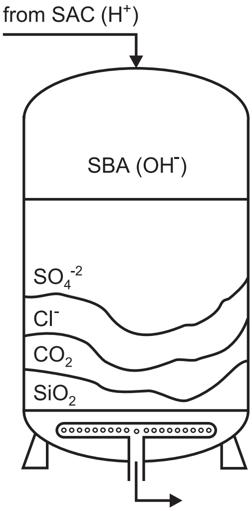
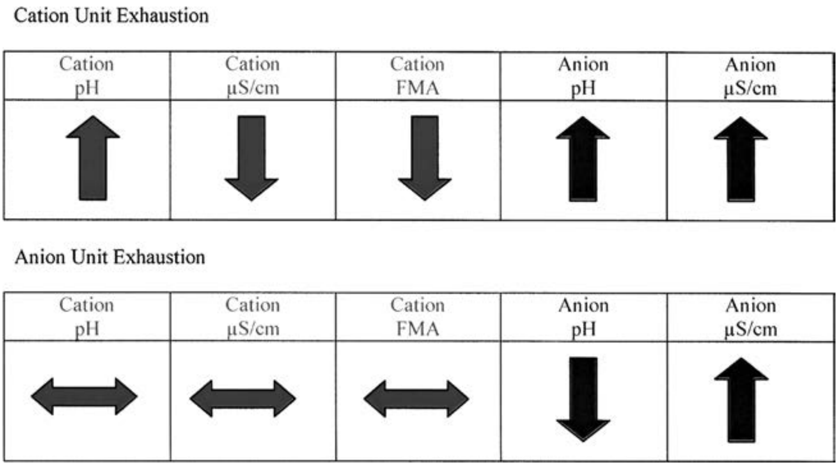


Figure 7.40 Breakthrough profile for SBA (OH^-) unit.

Figure 7.41 shows interpretation guidelines for SAC (H^+) and SBA (OH^-) units using the parameters discussed earlier.

Mixed-Bed Units

In a mixed-bed demineralizer, using both strong acid and strong base resins, similar reactions occur, but it is not possible to sample and test between the two exchange phases to determine which resin



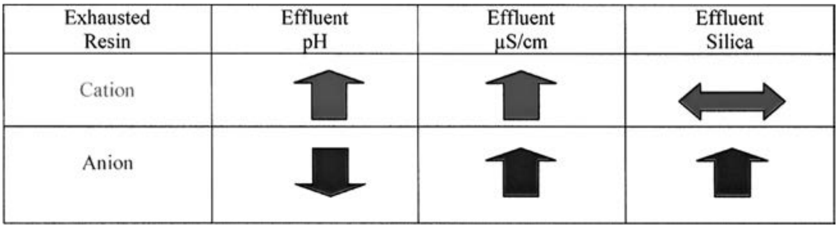
Cation Unit Exhaustion

Cation pH	Cation µS/cm	Cation FMA	Anion pH	Anion µS/cm
↑	↓	↓	↑	↑

Anion Unit Exhaustion

Cation pH	Cation µS/cm	Cation FMA	Anion pH	Anion µS/cm
↔	↔	↔	↓	↑

Figure 7.41 Demineralizer exhaustion interpretation guidelines (two-bed train operation).



Exhausted Resin	Effluent pH	Effluent µS/cm	Effluent Silica
Cation	↑	↑	↔
Anion	↓	↑	↑

Figure 7.42 Demineralizer exhaustion interpretation guidelines (mixed bed).

is exhausted. Figure 7.42 provides guidelines for correct diagnosis using the parameters discussed earlier.

Regenerants and Water

Besides breakthrough monitoring, the amount of service water each unit produces during each run, the amount of water needed for a complete regeneration cycle, and the amount of regenerant used should be monitored. Understanding trends in each of these parameters over time yields useful data and provides additional information as to when a unit needs remedial attention.

Chemical Cleaning

As discussed earlier, various contaminants may be present in waters that contact ion exchange resins. The annual resin analysis reveals contaminants and concentrations present. This information along with reduced quality service water, throughput capacity, or both, indicates whether it is necessary to consider cleaning the resin. Table 7.7 indicates some common foulants and cleaning solutions used to remove them. A proper procedure along with correct concentrations of cleaner is necessary before undertaking cleaning of any resin bed.

Evaluation of resin age, remaining capacity, expected restored capacity, chemical cleaning cost, and increased regenerant costs due to low throughput are all factors that need to be considered

Resin Type	Contaminant	Cleaning Solution
Mixed bed	Inorganics	HCl
SBA and WBA	Organics	NaCl with NaOH
SAC and WAC	$CaSO_4$	Sodium citrate
SBA and WBA	$CaSO_4$	HCl
SAC and SBA	Fe^{+3}	HCl

Table 7.7 Typical Cleaning Solutions to Remove Various Contaminants

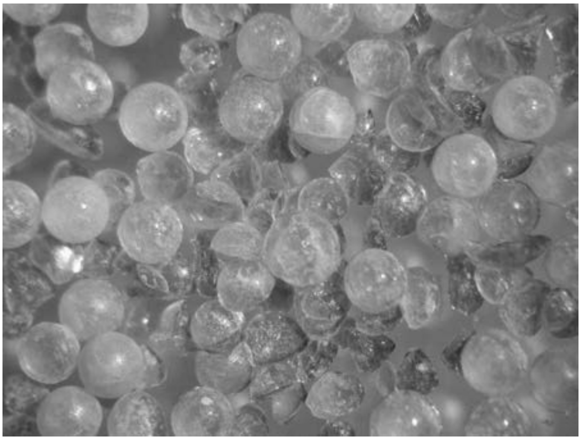


Figure 7.43 Organically fouled SBA resin before a brine squeeze.

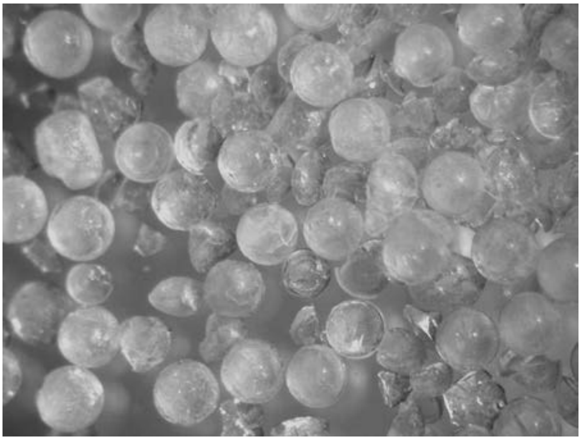


Figure 7.44 The same resin as shown in Fig. 7.43 after a successful brine squeeze was used to remove a large portion of the organics.

before undertaking resin cleaning. There is a balance point where replacement with new resin is less expensive if remaining capacity of existing resin has deteriorated significantly. Figures 7.43 and 7.44 illustrate the effect of a brine squeeze on an organically fouled anion resin.

Resin Storage

Most resin can be safely kept in wet storage for about two years, provided storage conditions are suitable. Resin should be stored in its original packaging between 32 to 86°F (0–30°C) in an interior location protected from container damage. Old resins that can be used to top up existing ion exchange beds require the same consideration.

Resin that undergoes several freeze/thaw cycles or becomes dry loses exchange capacity and even structural integrity. This shortens useful resin life.

Ion Exchange Equipment Configurations

Choosing the right equipment configuration, resin, and regenerant are largely dependent on required service water quality. Equipment is generally classified by the function the resin performs. Typical functions for water treatment are: softening (hardness removal), dealkalization (alkalinity removal), and demineralization (total ion removal). With the exception of simple hardness removal, there are many different equipment configurations and resin choices that can accomplish the task. Some common configurations are discussed below.

Softening

This process involves exchange of the scale forming cations calcium and magnesium for completely soluble sodium. It is most often utilized in treatment of surface and well water supplies for commercial, institutional, and industrial plants for process and boiler feedwater applications. Softening uses SAC (Na^+) resin, and regeneration may be co-current or counter-current in normal or packed bed units. However, when these units are used downstream of lime precipitation processes, only conventional co-current units that allow full backwash every regeneration are used. Producing soft wateris the simplest ion exchange process and is shown in Fig. 7.45. Figure 7.46 shows a typical water analysis for this type of ion exchange unit.

Dealkalizing

Alkalinity in boiler feedwater imposes limits on the number of times bulk boiler water can be concentrated before carryover is caused by foaming and priming. In addition, breakdown of alkalinity in the boiler releases free carbon dioxide that when redissolved in steam condensate forms carbonic acid, which is the cause of extensive return line corrosion. Accordingly, ion exchange systems that remove alkalinity are frequently used to pretreat boiler makeup water, even though boiler pressure does not dictate use of demineralization. Systems commonly used are:

- Chloride anion dealkalization—SBA (Cl^-)
- Weak acid dealkalization—WAC (H^+)
- Layered bed dealkalization—WAC (H^+)/SAC (Na^+)
- Split stream softening/dealkalization—SAC (H^+)/SAC (Na^+)

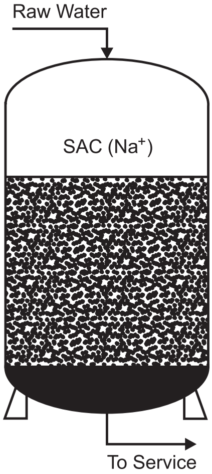
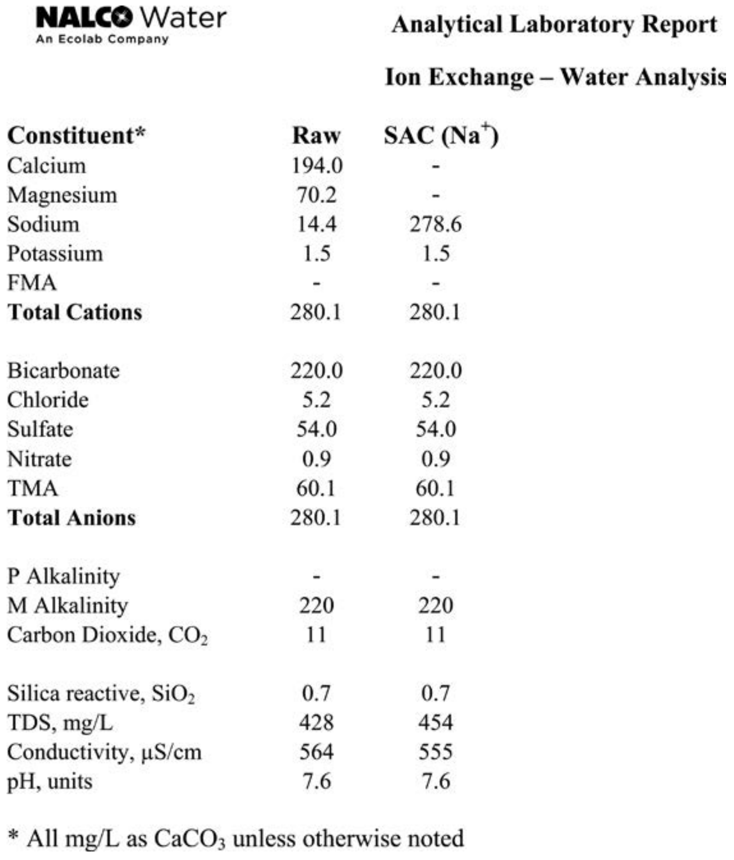


Figure 7.45 Typical softener arrangement.



Analytical Laboratory Report

Ion Exchange – Water Analysis

Constituent*	**Raw**	**SAC (Na^+)**
Calcium	194.0	-
Magnesium	70.2	-
Sodium	14.4	278.6
Potassium	1.5	1.5
FMA	-	-
Total Cations	280.1	280.1
Bicarbonate	220.0	220.0
Chloride	5.2	5.2
Sulfate	54.0	54.0
Nitrate	0.9	0.9
TMA	60.1	60.1
Total Anions	280.1	280.1
P Alkalinity	-	-
M Alkalinity	220	220
Carbon Dioxide, CO_2	11	11
Silica reactive, SiO_2	0.7	0.7
TDS, mg/L	428	454
Conductivity, µS/cm	564	555
pH, units	7.6	7.6

* All mg/L as $CaCO_3$ unless otherwise noted

Figure 7.46 Example water analyses for SAC (Na^+) softener.

Chloride Anion Dealkalization

This process is most often used in institutional and light industrial steam plants. Using a Type II SBA resin in chloride form is often seen as more desirable in plants that are not accustomed to handling large volumes of hazardous chemicals such as acids and caustics.

Anion influent must be completely softened to ensure hardness is not precipitated in the anion resin, and sodium chloride used for regeneration must be high purity with minimal hardness content.

While this process exchanges chloride for bicarbonate, carbonate, nitrate, phosphate, and sulfate, it does not exchange for silica. As such, it is unsuitable for use if downstream equipment has silica restrictions. This process does not reduce conductivity of treated effluent, and boiler blowdown is usually not reduced. Figure 7.47 illustrates this type of system. Figure 7.48 shows a typical water analysis.

Weak Acid Dealkalization

When used for dealkalization, WAC exchange and regeneration reactions occur at essentially stoichiometric levels. Since the process removes only hardness associated with alkalinity, some hardness remains in the effluent, and this must be removed by a SAC (Na^+) unit installed downstream. All ion exchange processes that use (H^+) resins, either SAC or WAC, are regenerated with strong mineral acids that destroy alkalinity, releasing free carbon dioxide, which is generally removed by forced draft atmospheric decarbonation or another process such as vacuum deaeration or gas transfer membranes.

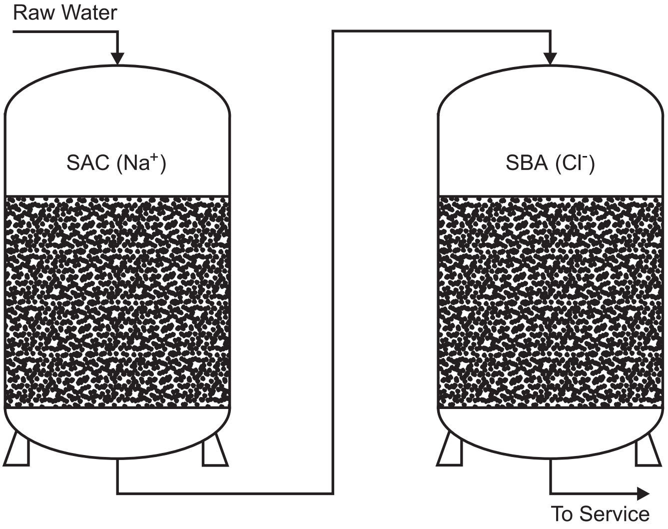
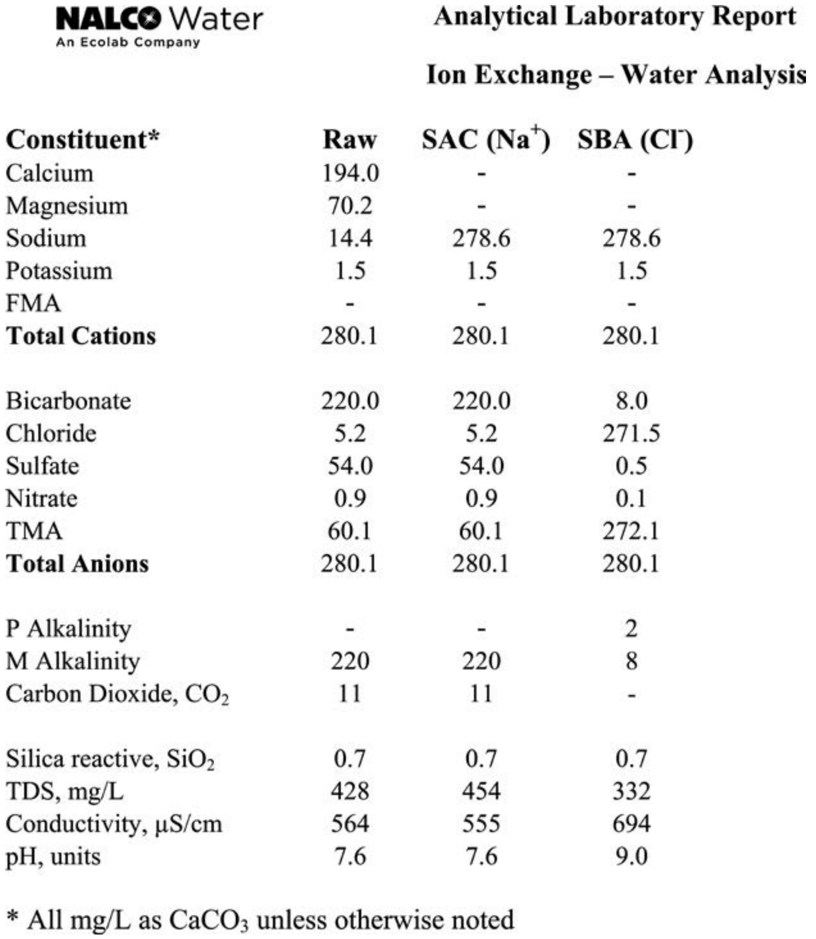


FIGURE 7.47 Typical chloride dealkalizer arrangement.



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Ion Exchange – Water Analysis

Constituent*	Raw	SAC (Na^+)	SBA (Cl^-)
Calcium	194.0	-	-
Magnesium	70.2	-	-
Sodium	14.4	278.6	278.6
Potassium	1.5	1.5	1.5
FMA	-	-	-
Total Cations	280.1	280.1	280.1
Bicarbonate	220.0	220.0	8.0
Chloride	5.2	5.2	271.5
Sulfate	54.0	54.0	0.5
Nitrate	0.9	0.9	0.1
TMA	60.1	60.1	272.1
Total Anions	280.1	280.1	280.1
P Alkalinity	-	-	2
M Alkalinity	220	220	8
Carbon Dioxide, CO_2	11	11	-
Silica reactive, SiO_2	0.7	0.7	0.7
TDS, mg/L	428	454	332
Conductivity, µS/cm	564	555	694
pH, units	7.6	7.6	9.0

* All mg/L as $CaCO_3$ unless otherwise noted

Figure 7.48 Example water analyses for chloride dealkalizer.

This process reduces TDS and specific conductance of treated water. After reduction of carbon dioxide to 5 to 10 mg/L with a decarbonator (Fig. 7.49), the pH is about 6.0, and the effluent is nonscale forming. The pH is usually adjusted to 8.3 to 10.2 by feeding caustic (NaOH) on a controlled basis to the sump of the decarbonator. Figure 7.50 illustrates this type of system. Figure 7.51 shows a typical water analysis for this type of unit.

Layered Bed Dealkalization

A less common type of WAC dealkalizer is a layered unit with WAC (H^+) resin installed on top of SAC (Na^+) resin, so that alkalinity removal and complete softening are accomplished in one vessel.

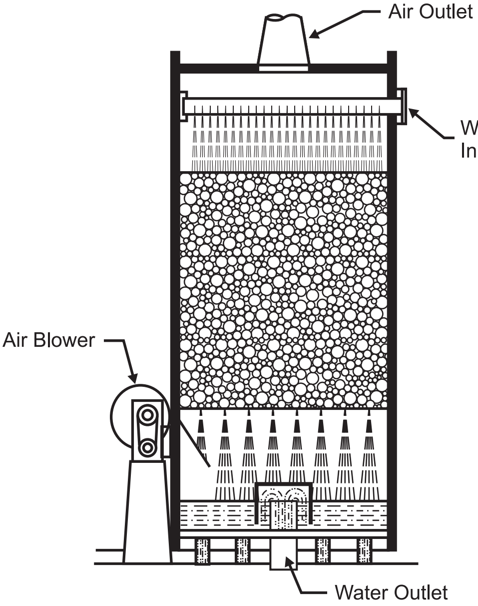


Figure 7.49 Typical decarbonator or degassifier.

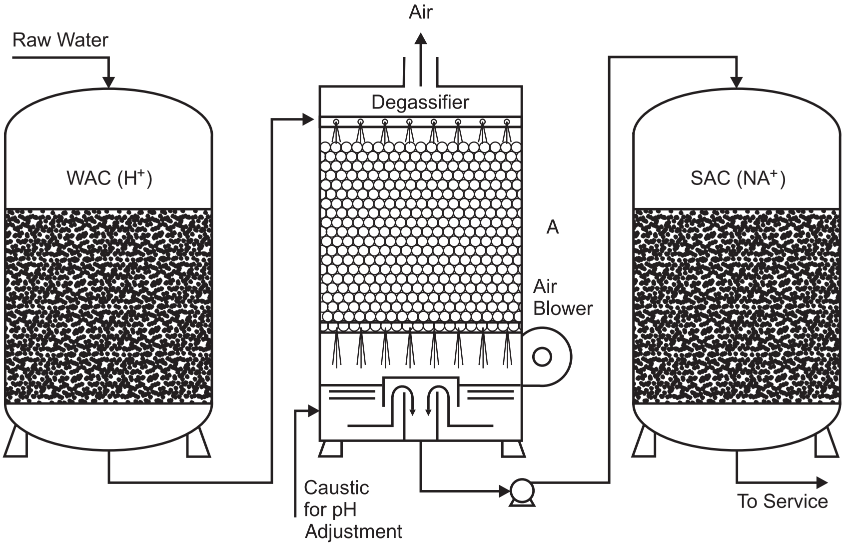
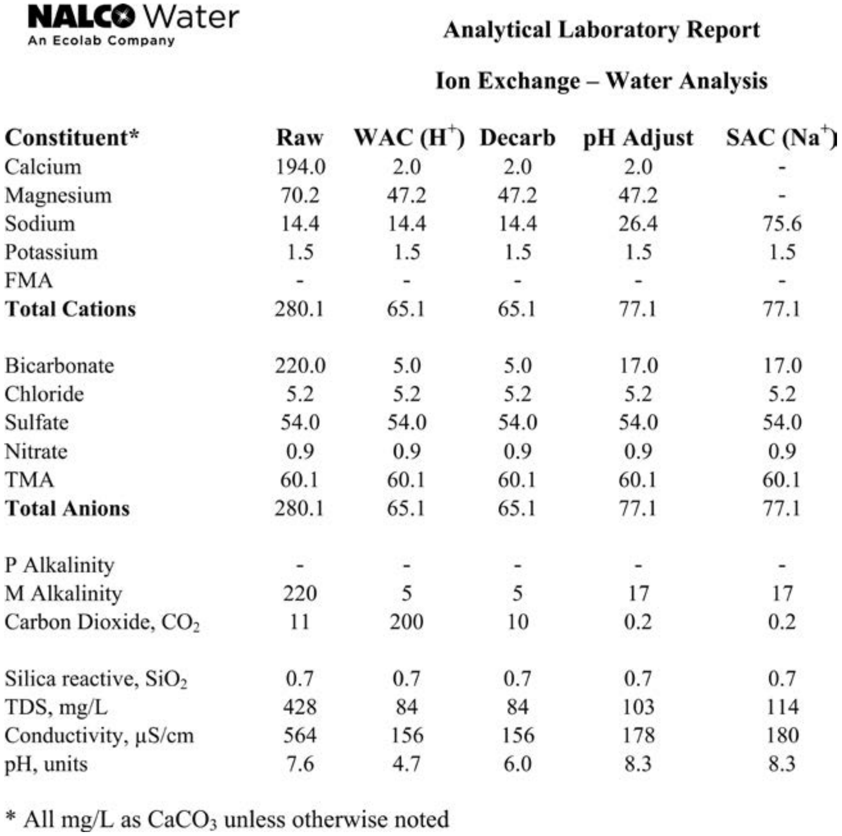


Figure 7.50 WAC (H^+) with caustic adjustment.



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Ion Exchange – Water Analysis

Constituent*	**Raw**	**WAC (H^+)**	**Decarb**	**pH Adjust**	**SAC (Na^+)**
Calcium	194.0	2.0	2.0	2.0	-
Magnesium	70.2	47.2	47.2	47.2	-
Sodium	14.4	14.4	14.4	26.4	75.6
Potassium	1.5	1.5	1.5	1.5	1.5
FMA	-	-	-	-	-
Total Cations	280.1	65.1	65.1	77.1	77.1
Bicarbonate	220.0	5.0	5.0	17.0	17.0
Chloride	5.2	5.2	5.2	5.2	5.2
Sulfate	54.0	54.0	54.0	54.0	54.0
Nitrate	0.9	0.9	0.9	0.9	0.9
TMA	60.1	60.1	60.1	60.1	60.1
Total Anions	280.1	65.1	65.1	77.1	77.1
P Alkalinity	-	-	-	-	-
M Alkalinity	220	5	5	17	17
Carbon Dioxide, CO_2	11	200	10	0.2	0.2
Silica reactive, SiO_2	0.7	0.7	0.7	0.7	0.7
TDS, mg/L	428	84	84	103	114
Conductivity, µS/cm	564	156	156	178	180
pH, units	7.6	4.7	6.0	8.3	8.3

* All mg/L as $CaCO_3$ unless otherwise noted

Figure 7.51 Example water analyses for WAC dealkalization with caustic adjustment.

Chemical reactions are the same as previously discussed for both resins. Success of this process depends greatly on the two resins remaining in discrete layers.

Such units are first regenerated with a starvation or small excess acid dosage that is passed downflow through both resins. Hardness ions regenerated from WAC resin contact the SAC resin layer, fully exhausting that layer. A high regeneration dosage of sodium chloride brine is then passed downflow through both resins regenerating only the SAC layer in the bottom of the unit. Figure 7.52 illustrates this type of system. Figure 7.53 shows a typical water analysis for this type of unit.

Split Stream Softening/Dealkalization

Split stream dealkalization makes use of both a SAC (H^+) and a SAC (Na^+) unit operating in parallel and then blending the effluents to obtain desired alkalinity. A calculable percentage of the full treatment flow is softened by SAC (Na^+) units, with the effluent

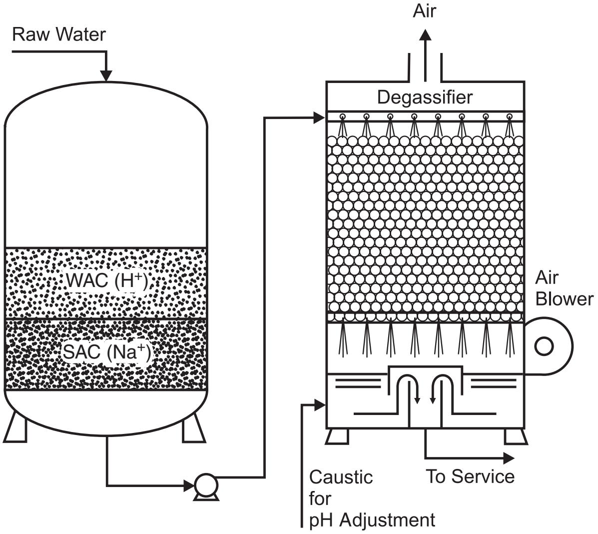
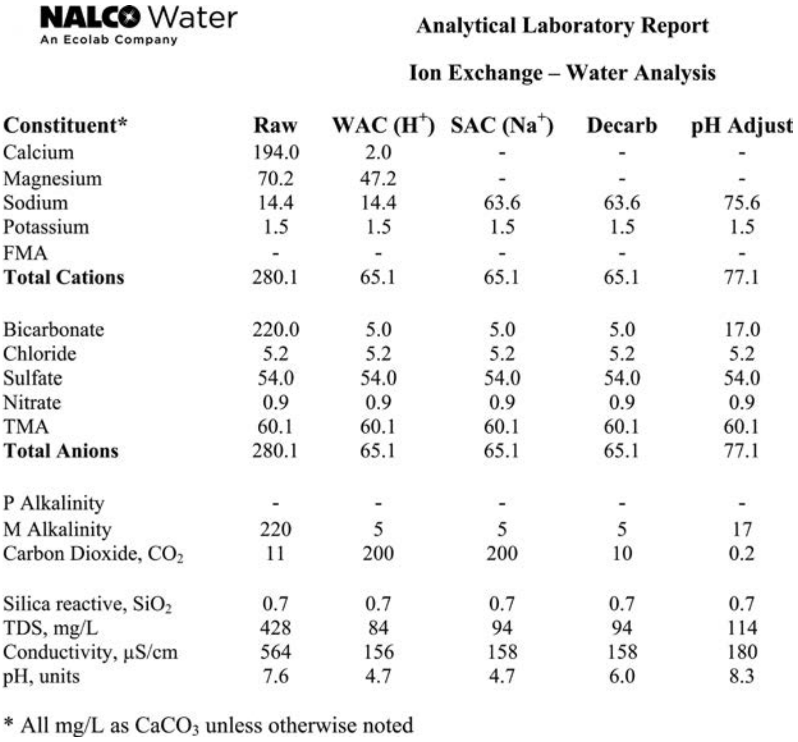


Figure 7.52 Layered bed dealkalization arrangement.



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Ion Exchange – Water Analysis

Constituent*	**Raw**	**WAC (H^+)**	**SAC (Na^+)**	**Decarb**	**pH Adjust**
Calcium	194.0	2.0	-	-	-
Magnesium	70.2	47.2	-	-	-
Sodium	14.4	14.4	63.6	63.6	75.6
Potassium	1.5	1.5	1.5	1.5	1.5
FMA	-	-	-	-	-
Total Cations	280.1	65.1	65.1	65.1	77.1
Bicarbonate	220.0	5.0	5.0	5.0	17.0
Chloride	5.2	5.2	5.2	5.2	5.2
Sulfate	54.0	54.0	54.0	54.0	54.0
Nitrate	0.9	0.9	0.9	0.9	0.9
TMA	60.1	60.1	60.1	60.1	60.1
Total Anions	280.1	65.1	65.1	65.1	77.1
P Alkalinity	-	-	-	-	-
M Alkalinity	220	5	5	5	17
Carbon Dioxide, CO_2	11	200	200	10	0.2
Silica reactive, SiO_2	0.7	0.7	0.7	0.7	0.7
TDS, mg/L	428	84	94	94	114
Conductivity, µS/cm	564	156	158	158	180
pH, units	7.6	4.7	4.7	6.0	8.3

* All mg/L as $CaCO_3$ unless otherwise noted

Figure 7.53 Example water analyses for layered bed dealkalization.

containing full M alkalinity. This is blended with the remaining percentage of flow treated in SAC (H^+) units with the effluent containing FMA but essentially free of calcium and magnesium hardness. The blended water M alkalinity in the SAC (Na^+) effluent is reduced to a chosen residual by FMA in the SAC (H^+) effluent, releasing carbon dioxide (see Fig. 7.54).

Equation (7.39) is used to calculate the ratio of SAC (H^+) flow to SAC (Na^+) flow.

$$\%\ \mathrm{SAC}\ (\mathrm{H}^+) = \frac{100(\mathrm{Alk}_i - \mathrm{Alk}_f)}{\mathrm{Alk}_i + \mathrm{FMA}} \tag{7.39}$$

where % SAC (H^+) = SAC (H^+) flow rate, percent of total flow rate
Alk_i = influent water alkalinity, mg/L as $CaCO_3$
Alk_f = desired alkalinity after blending, mg/L as $CaCO_3$
FMA = free mineral acidity in SAC (H^+) effluent, mg/L as $CaCO_3$

With the split stream process and blending of SAC (H^+) and SAC (Na^+) effluents, sodium leakage is of no consequence. Success of this form of dealkalization is largely dependent on accurate response of the blending system for flow measurement and ratio control. Simple flow control may be inaccurate if the total blended system flow rate varies considerably. For this reason and to ensure that water containing FMA is not discharged to boiler feedwater, it is strongly recommended that positive M alkalinity be maintained at more than 10 mg/L as $CaCO_3$. Following blending of the two streams, free carbon dioxide must be removed to elevate the pH.

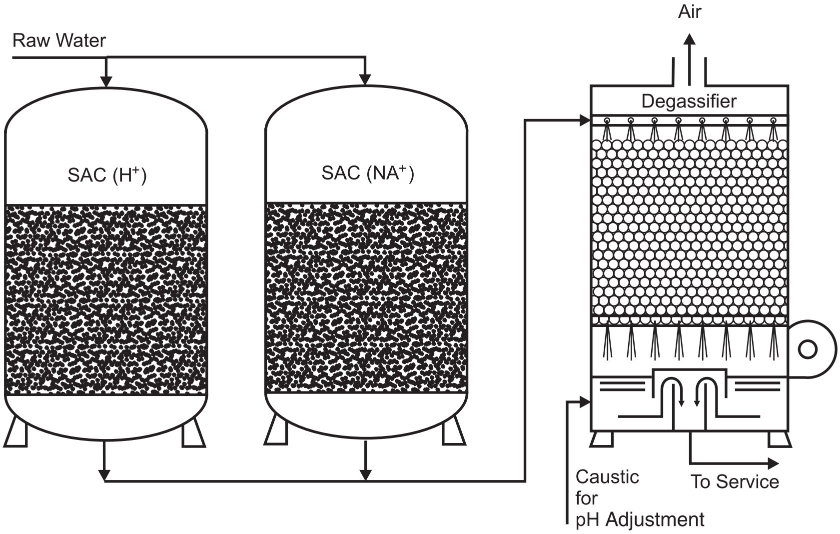
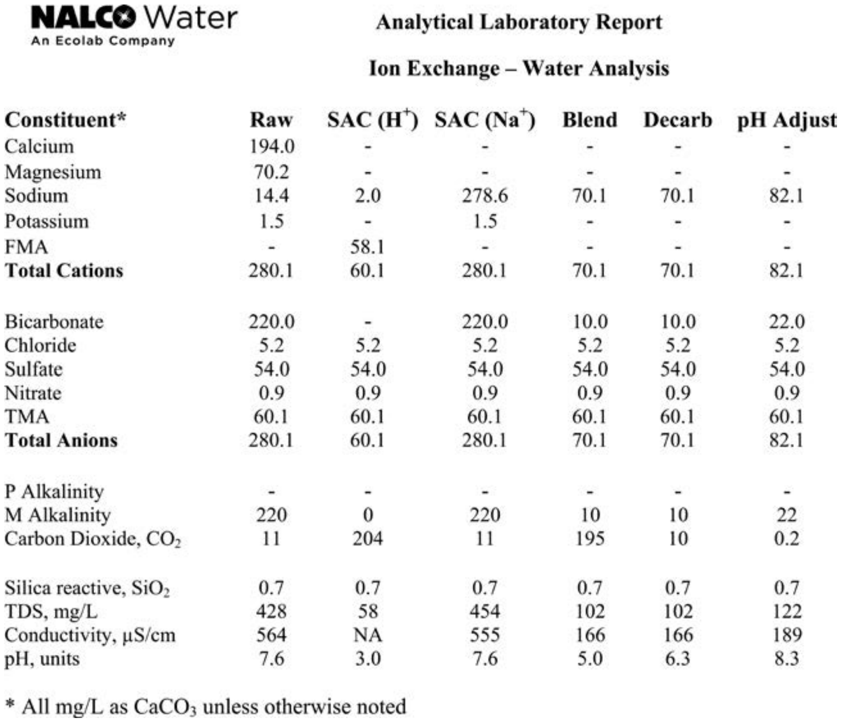


FIGURE 7.54 Split stream softening and dealkalization.



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Ion Exchange – Water Analysis

Constituent*	Raw	SAC (H$^+$)	SAC (Na$^+$)	Blend	Decarb	pH Adjust
Calcium	194.0	-	-	-	-	-
Magnesium	70.2	-	-	-	-	-
Sodium	14.4	2.0	278.6	70.1	70.1	82.1
Potassium	1.5	-	1.5	-	-	-
FMA	-	58.1	-	-	-	-
Total Cations	280.1	60.1	280.1	70.1	70.1	82.1
Bicarbonate	220.0	-	220.0	10.0	10.0	22.0
Chloride	5.2	5.2	5.2	5.2	5.2	5.2
Sulfate	54.0	54.0	54.0	54.0	54.0	54.0
Nitrate	0.9	0.9	0.9	0.9	0.9	0.9
TMA	60.1	60.1	60.1	60.1	60.1	60.1
Total Anions	280.1	60.1	280.1	70.1	70.1	82.1
P Alkalinity	-	-	-	-	-	-
M Alkalinity	220	0	220	10	10	22
Carbon Dioxide, CO_2	11	204	11	195	10	0.2
Silica reactive, SiO_2	0.7	0.7	0.7	0.7	0.7	0.7
TDS, mg/L	428	58	454	102	102	122
Conductivity, µS/cm	564	NA	555	166	166	189
pH, units	7.6	3.0	7.6	5.0	6.3	8.3

* All mg/L as $CaCO_3$ unless otherwise noted

Figure 7.55 Example water analysis for split stream softening/dealkalization.

This process reduces TDS and specific conductance of treated water. After reduction of carbon dioxide to 5 to 10 mg/L, the decarbonator effluent pH is about 6.3 and is nonscale forming. It is usual to adjust the pH to 8.3 to 10.2 by feeding caustic on a controlled basis to the clearwell of the degassifier. Figure 7.55 shows a typical water analysis from a split stream unit.

Primary Demineralizing

Demineralization is the process of removing virtually all dissolved solids from water and producing essentially pure water. Demineralized water is used for a variety of purposes:

- Boiler makeup for industrial and utility units of many types with a broad range of operating pressures, even into the supercritical range
- Process water used in a wide variety of diverse manufacturing operations that can include integration of water into a manufactured product

- High-purity rinse water used to eliminate performance defects, such as in the manufacture of computer chips, where water must have specific conductance less than 0.055 µS/cm or a resistance greater than 18.2 MΩ

Ion exchange units used for demineralization must include both cation and anion exchange processes. Just about any configuration of equipment is possible and is usually determined by raw water characteristics, capital expenditure, and regeneration costs. Following are several common designs.

Conventional Twin-Bed Demineralization

The two component pieces of this type of demineralization are a SAC (H^+) unit that removes all cations followed by a SBA (OH^-) unit that removes all anions. Resulting service water is very close to neutral pH with extremely low conductivity. Although not necessary, there is usually a decarbonator between the cation and anion units. This reduces carbon dioxide loading on the anion bed, and thus, a corresponding reduction in resin and regenerant for the anion unit is possible. In low alkalinity raw waters, a decarbonator is generally omitted, as there is little benefit to offset the capital cost. Anion and cation units are matched so that each exhausts at approximately the same time. This type of sizing allows for a "train" or "set" of exchangers to go into and out of service together. Figure 7.56 illustrates this type of system. Figure 7.57 shows a typical water analysis for this type of ion exchange unit.

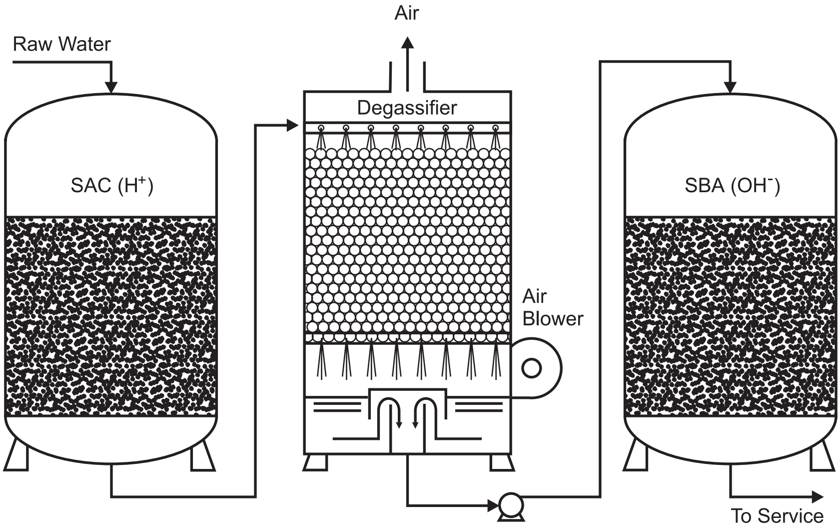
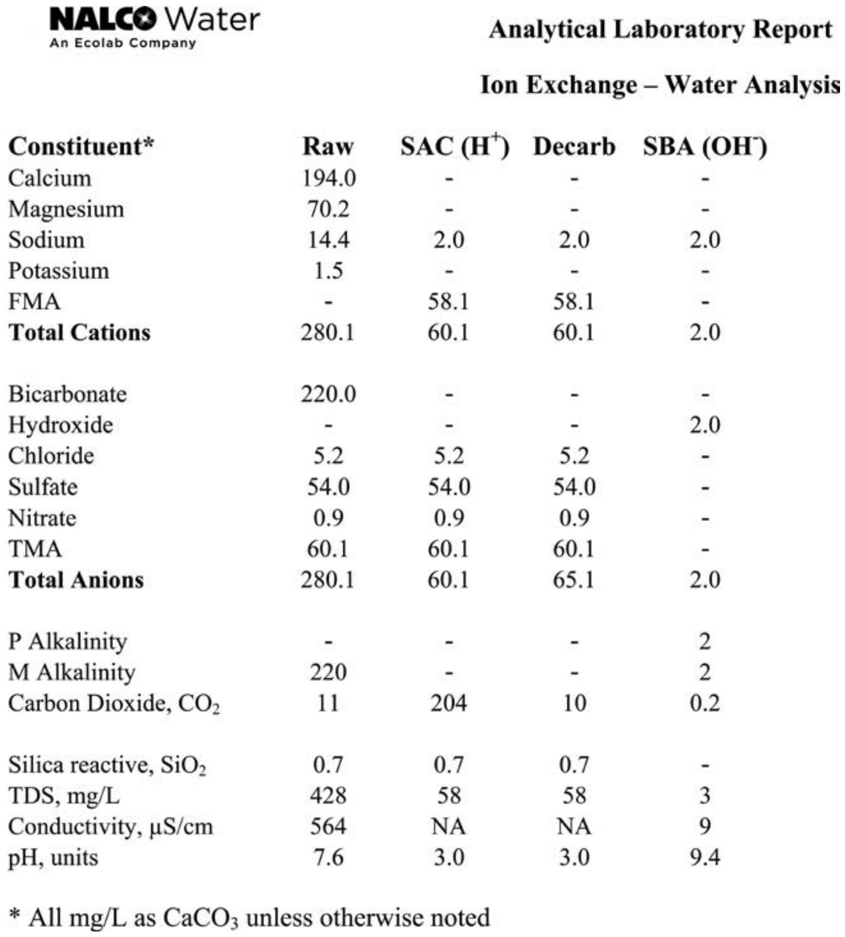


Figure 7.56 Twin-bed demineralization with decarbonation.



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Ion Exchange – Water Analysis

Constituent*	Raw	SAC (H^+)	Decarb	SBA (OH^-)
Calcium	194.0	-	-	-
Magnesium	70.2	-	-	-
Sodium	14.4	2.0	2.0	2.0
Potassium	1.5	-	-	-
FMA	-	58.1	58.1	-
Total Cations	280.1	60.1	60.1	2.0
Bicarbonate	220.0	-	-	-
Hydroxide	-	-	-	2.0
Chloride	5.2	5.2	5.2	-
Sulfate	54.0	54.0	54.0	-
Nitrate	0.9	0.9	0.9	-
TMA	60.1	60.1	60.1	-
Total Anions	280.1	60.1	65.1	2.0
P Alkalinity	-	-	-	2
M Alkalinity	220	-	-	2
Carbon Dioxide, CO_2	11	204	10	0.2
Silica reactive, SiO_2	0.7	0.7	0.7	-
TDS, mg/L	428	58	58	3
Conductivity, µS/cm	564	NA	NA	9
pH, units	7.6	3.0	3.0	9.4

* All mg/L as $CaCO_3$ unless otherwise noted

Figure 7.57 Example water analyses for SAC (H^+)-decarbonator-SBA (OH^-).

Twin-Bed Demineralization with WAC (H^+)

If raw water contains very high hardness and alkalinity, utilizing a WAC (H^+) unit in front of the SAC (H^+) unit helps reduce load to the strong acid unit. Since the WAC (H^+) unit removes both alkalinity and associated hardness, the SAC (H^+) unit is not taxed with these ions and is thus better equipped to polish the WAC (H^+) effluent. Decarbonation is necessary before effluent passes to the SBA (OH^-) unit. Figure 7.58 illustrates this type of system. Figure 7.59 shows a typical water analysis for this type of ion exchange unit.

Twin-Bed Demineralization with WBA (OH^-)

Many organics, but not all, detected by methods such as total organic carbon (TOC) in raw surface waters are a problem in demineralizers.

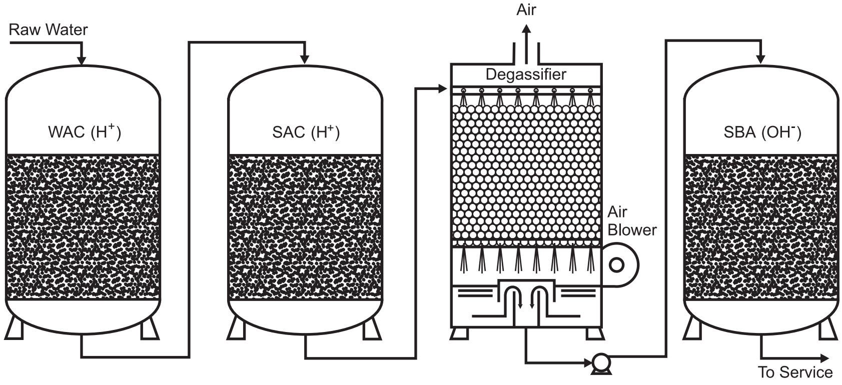
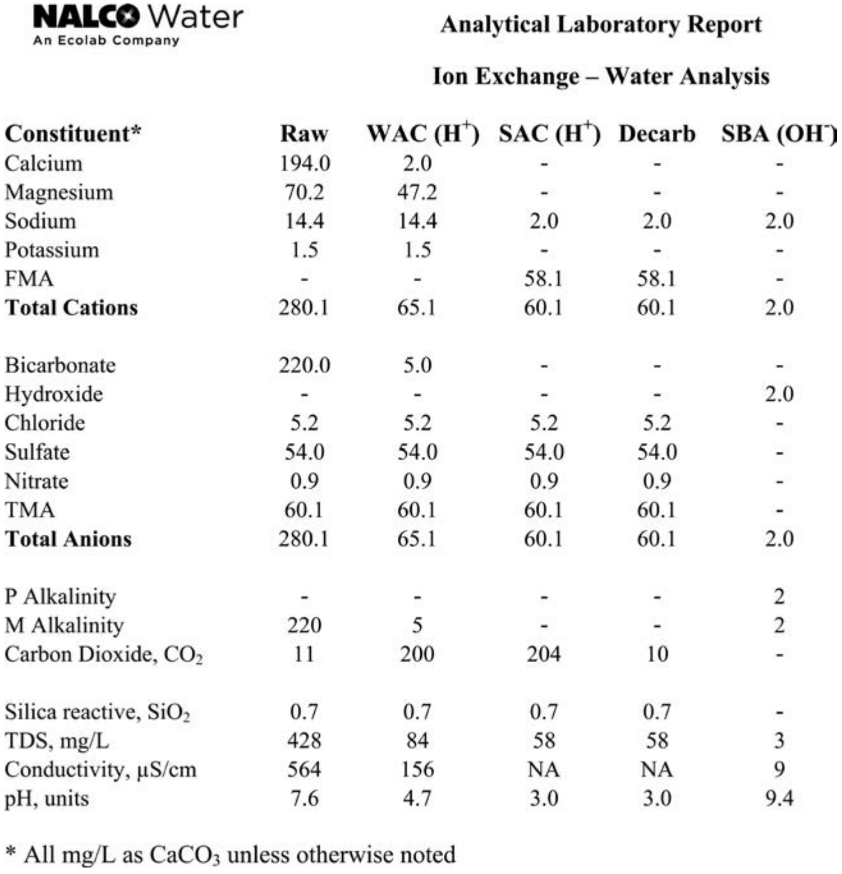


Figure 7.58 Twin-bed demineralization with a WAC (H^+) for high hardness and alkalinity waters.



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Ion Exchange – Water Analysis

Constituent*	**Raw**	**WAC (H^+)**	**SAC (H^+)**	**Decarb**	**SBA (OH^-)**
Calcium	194.0	2.0	-	-	-
Magnesium	70.2	47.2	-	-	-
Sodium	14.4	14.4	2.0	2.0	2.0
Potassium	1.5	1.5	-	-	-
FMA	-	-	58.1	58.1	-
Total Cations	280.1	65.1	60.1	60.1	2.0
Bicarbonate	220.0	5.0	-	-	-
Hydroxide	-	-	-	-	2.0
Chloride	5.2	5.2	5.2	5.2	-
Sulfate	54.0	54.0	54.0	54.0	-
Nitrate	0.9	0.9	0.9	0.9	-
TMA	60.1	60.1	60.1	60.1	-
Total Anions	280.1	65.1	60.1	60.1	2.0
P Alkalinity	-	-	-	-	2
M Alkalinity	220	5	-	-	2
Carbon Dioxide, CO_2	11	200	204	10	-
Silica reactive, SiO_2	0.7	0.7	0.7	0.7	-
TDS, mg/L	428	84	58	58	3
Conductivity, µS/cm	564	156	NA	NA	9
pH, units	7.6	4.7	3.0	3.0	9.4

* All mg/L as $CaCO_3$ unless otherwise noted

Figure 7.59 Example water analyses for WAC (H^+)-SAC (H^+)-decarbonator-SBA (OH^-).

Naturally occurring fulvic and humic acids present the greatest threat to continued production of high-purity demineralized water. These are present as the product of decayed vegetation (leaves, grasses, moss, etc.) with which surface waters come into contact. In many cases, these organics can foul SBA resin. Color in water is a good indication that organic fouling potential exists, but color bodies may be absent while organic acid concentrations are sufficient to cause severe fouling of SBA (OH^-) resins. This is particularly true in low TDS waters such as encountered in mountainous coastal regions.

Organic acids poison, or foul, SBA (OH^-) resins but do not cause the same effect when systems use WBA (OH^-) resin. Organic acids are absorbed into the resin skeleton of SBA (OH^-) and block ion exchange sites. This fouling is usually only partially reversible and results in shortened service throughputs, higher operating costs for regeneration, high labor and chemical costs for resin cleaning, high resin replacement costs, lower treated effluent purity, and high wastewater generation.

One approach to remove these organics is to trap them with a WBA unit. The advantage of this approach is that effluent water for this unit does not affect exchange capacity of SBA units that follow. Organics are caught on the WBA and are not passed through to the SBA. Figure 7.60 illustrates this type of system. Figure 7.61 shows a typical water analysis for this type of ion exchange unit.

Mixed-Bed Demineralizing

Mixed-bed demineralizers contain two resins, SAC (H^+) and SBA (OH^-), which are homogeneously mixed when in service. When exhausted, resin components are separated by backwashing. Due to density difference between the two resins, SAC (H^+) resin remains on the bottom while SBA (OH^-) resin rests on top. Each resin is regenerated separately with appropriate regenerant. After regeneration and rinsing,

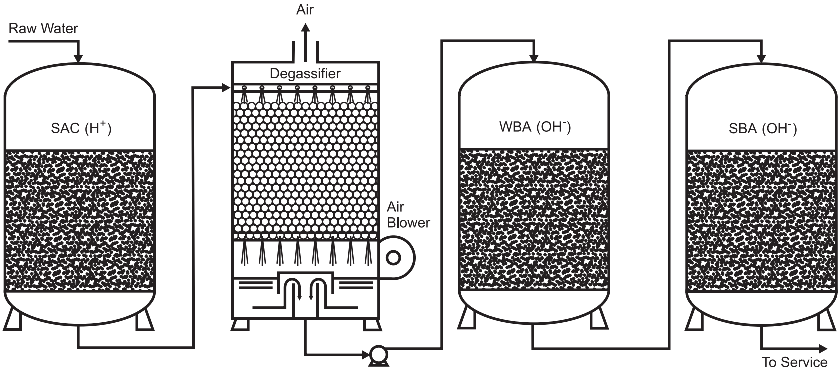
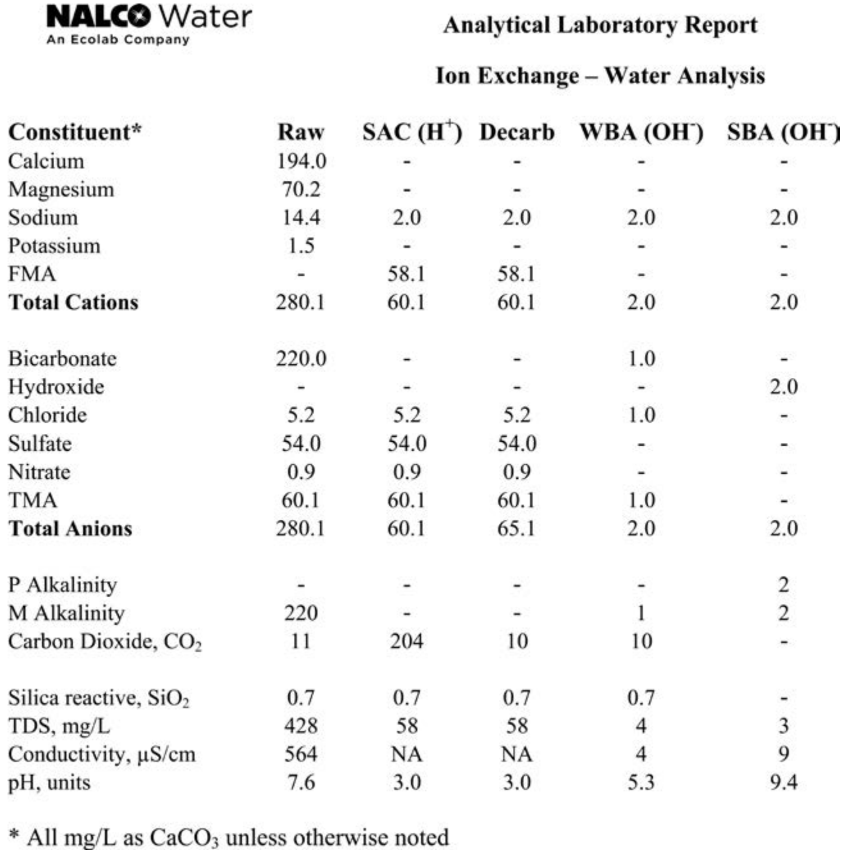


Figure 7.60 Organic trap using WBA (OH^-) in a twin bed train.



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Ion Exchange – Water Analysis

Constituent*	**Raw**	**SAC (H^+)**	**Decarb**	**WBA (OH^-)**	**SBA (OH^-)**
Calcium	194.0	-	-	-	-
Magnesium	70.2	-	-	-	-
Sodium	14.4	2.0	2.0	2.0	2.0
Potassium	1.5	-	-	-	-
FMA	-	58.1	58.1	-	-
Total Cations	280.1	60.1	60.1	2.0	2.0
Bicarbonate	220.0	-	-	1.0	-
Hydroxide	-	-	-	-	2.0
Chloride	5.2	5.2	5.2	1.0	-
Sulfate	54.0	54.0	54.0	-	-
Nitrate	0.9	0.9	0.9	-	-
TMA	60.1	60.1	60.1	1.0	-
Total Anions	280.1	60.1	65.1	2.0	2.0
P Alkalinity	-	-	-	-	2
M Alkalinity	220	-	-	1	2
Carbon Dioxide, CO_2	11	204	10	10	-
Silica reactive, SiO_2	0.7	0.7	0.7	0.7	-
TDS, mg/L	428	58	58	4	3
Conductivity, µS/cm	564	NA	NA	4	9
pH, units	7.6	3.0	3.0	5.3	9.4

* All mg/L as $CaCO_3$ unless otherwise noted

Figure 7.61 Example water analyses for SAC (H^+)-decarbonator-WBA (OH^-)-SBA (OH^-).

resins are remixed using air injected through the underdrain. A final rinse returns the unit to service producing very high-purity effluent.

Effectiveness of separation and remixing are crucial to performance in these units. Resin separation is enhanced by the use of resins with special properties such as UPS and particle density. Another option is the use of a narrow inert resin layer that rests between the two active resins after separation. Air mixing is optimized by reducing the head of water over the resin bed to a desired, constant level for all regenerations.

These units operate either as primary treatment when raw water has very low TDS or more commonly as a polishing unit after primary demineralization. Experience shows that only polishing mixed bed demineralizers are consistently capable of producing the purity of water required for microchip manufacturing, provided proper pretreatment is included upstream.

Chemical reactions are the same as previously described for SAC (H^+) and SBA (OH^-) resins in separate units but with very important differences. In separate beds, the SAC (H^+) reaction creates FMA from sulfate, chloride, phosphate, and nitrate ions in the water. These strong mineral acids, even at low concentration, are sufficient to create an acidic environment that elutes sodium ions (leakage) into the effluent. When combined with free hydroxide from the SBA (OH^-) forming NaOH, conductivity of the final effluent is increased.

In a mixed bed, mineral acid created by a SAC (H^+) bead is immediately converted to water by the adjacent SBA (OH^-) bead, maintaining a neutral environment around the bead. The acid environment is eliminated, and sodium leakage is reduced. In addition, in the favorable kinetics of a mixed bed, the SBA (OH^-) leakage is chloride not hydroxide. 1 mg/L of sodium chloride, expressed as $CaCO_3$, contributes 2.5 µS/cm specific conductance to the effluent. As a properly designed and operated mixed bed, even in primary service, can produce water containing 0.2 to 0.5 mg/L sodium as $CaCO_3$, effluent specific conductance may be 0.5 to 1.25 µS/cm. In polishing service, with adequately pretreated influent, mixed beds can produce effluent containing less than 0.022 mg/L sodium and specific conductance below 0.055 µS/cm (Fig. 7.62).

Packed Bed Units

This type of unit operates with the vessel virtually full, or packed, with working resin as opposed to the nearly 50% of the internal vessel volume being open "freeboard" space as it is in a conventionally designed unit. Normally, a layer of inert resin is also used, and the combined bed is sandwiched between upper and lower collector/distributor systems, called nozzle plates, complete with strainers. Total depth of working resin in its maximum swollen state plus inert

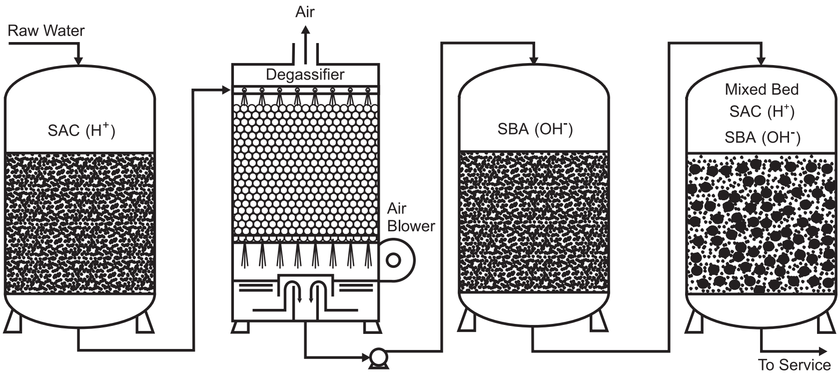

FIGURE 7.62 Mixed-bed polishing demineralizer.

resin is calculated to leave about 2 inches (51 mm) freeboard. In cases where actual resin swelling does not occur to the extent predicted by the resin manufacturer, excess freeboard and resin fluidization can yield off-specification water.

The concept of such designs is to reduce wastewater generation, and a major feature is to eliminate backwashing and to save rinse water by recirculating within the system. In most of these systems, resin cannot be backwashed in situ and must be transferred to an external tank when backwashing is necessary. In order to achieve this goal, influent, service water, and regenerants must be extremely clean and free of particulates and microorganisms that can cause plugging or fouling and thus create a need to backwash.

Resins used are UPS, and regeneration is counter-current. There are multiple, competitive equipment designs available. Some are downflow service with upflow regeneration, and some are the opposite with upflow service and downflow regeneration.

Some systems are designed so that a single unit contains two distinctly separate resin chambers, each containing a different resin with thoroughfare regeneration of both using a common regenerant. Chamber separation may be a solid diaphragm, called a nozzle plate, through which are installed double ended strainer assemblies with a strainer in either chamber. The water and regenerant solutions pass from one chamber to another through these interconnecting strainers. Alternately, mechanical separation may be a flat panel of perforated alloy well screen (Fig. 7.63).

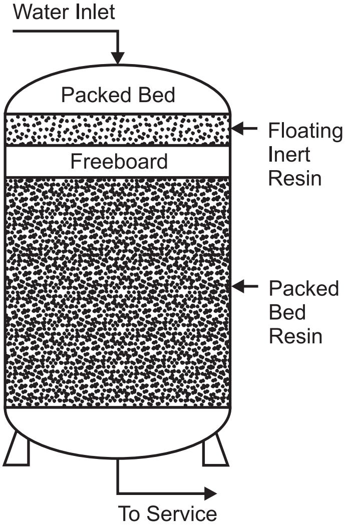

Figure 7.63 Typical packed bed arrangement.

Water Use Optimization Strategies

Many industrial plants are located where they are because of the ready access to large volumes of good quality water. Other plants simply tap into city or other municipal water sources. Either way the ion exchange processes in use in these plants are rarely especially larger water consumers. But even so these plants may still seek strategies to minimize water use as a starting point, and wastewater generation more specifically. There are typically two different approaches considered when looking to reduce water in the pretreatment plant:

1. System optimization
2. Water recovery

System Optimization

Regeneration optimization is typically the approach taken when trying to minimizing water utilization in the pretreatment systems. There are four areas where optimization and preventative maintenance can help minimize your water consumption:

1. Regeneration optimization
2. Throughput capacity
3. Regeneration versus throughput
4. Resin quality and quantity

Regeneration optimization is a balance between the amount of regenerant used per ft^3(L) of resin and the tolerable ionic leakage from the vessel. There is a sweet spot for each type of resin and regenerant that provides optimal regeneration. Too little regenerant yields poorer quality water and increased regenerations, too much regenerant starts to flattens the performance curve and doesn't provide the corresponding kgr/ft^3 (g/L) removal capacity. Optimizing the regenerant to provide long throughput capacity minimizes regeneration cycles and improves water quality

Monitoring throughput capacity is an excellent way of determining variability in service run lengths necessity increased regeneration cycles. Utilization of water meters to determine actual service run length is important. There are two comparisons to draw when evaluating service runs. The first is run length against historical run length, while the second is against theoretical or expected length. These comparisons will illuminate the performance of the ion exchange process and can indicate if there are issues that require attention.

Evaluating the amount of water utilized in the regeneration process against throughput capacity is a measure that can be utilized to determine excessive water usage in regeneration. Regeneration water should be in the 3 to 5% of throughput. If above this level, evaluation of the regeneration process will be necessary to determine where the excess water is being utilized.

Many plants do not put into practice a good resin management program. As such, when resin failure occurs, it can be a shock to the maintenance budget. Long before resin failure occurs however, there are indications of shortened throughput, increased regeneration cycles, ionic leakage and the like. All of which increase water utilization in the ion exchange plant. There are several key components in a resin management program. When taken together, they offer a clear picture of expected resin life, total operating cost, performance expectations, and cleaning cycles. Component pieces of a resin management program are: expected length of service, annual resin analysis, annual regeneration profile, monitoring service performance, chemical cleaning, and resin storage. Keeping your resin in good operation condition helps minimize the wastage of water in general.

Water Recovery

The only part of the regeneration process where the water flow could possibly be reused or recycled would be the final or fast rinse of the regeneration process. And even this stream would have a somewhat variable ionic content making its reuse or recovery questionable except under the best controlled circumstances. Using conductivity as a measure of ionic content may be the best way to on-line test a stream to initiate a recovery process. But even so, the economics of these recovery processes are rarely favorable. The piping needed to recovery this water would have to be corrosion resistant in most cases, and therefore quite expensive. Depending on where the recovered water might be used determines the length of the piping run and therefore its cost. Given the intermittent nature of regeneration processes most plants would want to collect the recovered water into a tank and then release it into its point of reuse on a more gradual basis. This makes managing that volume of water in the storage tank to be a considerable challenge, for very little economic benefit. As a result of these concerns and drawbacks water reuse and recovery from the ion exchange process is something rarely seen in industrial systems today.

CHAPTER 8

Membrane Separation

Membrane processes have been around since the early 1900s when Bechhold developed the first ultrafilter cir. 1907.[1] By the 1920s and 1930s, both microfiltration (MF) and ultrafiltration (UF) membranes were popular for laboratory applications. Industrial applications of MF and UF began in the early 1960s and 1970s, about the same time that Loeb and Sourirajan developed the "skinned," cellulose acetate reverse osmosis (RO) membrane (1960) that became the first commercially-viable RO membranes installed in Coalinga, CA (1965).[2] Later, it was the development of the polyamide, thin-film composite (TFC®) RO membrane by Cadotte in 1972 that allowed relatively higher flux and rejection that gave RO membranes broad appeal.[3] Since that time, a host of membrane-based separation technologies have been developed for specific applications. This chapter covers some of the most popular membrane technologies applied today:

- **Microfiltration (MF)**: suspended solids filtration
- **Ultrafiltration (UF)**: finer suspended solids filtration
- **Nanofiltration (NF)**: demineralization of multivalent ions
- **Reverse Osmosis (RO)**: demineralization of monovalent ions
- **Continuous Electrodeionization (CEDI)**: demineralization polishing

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[1] Baker, R., *Membrane Technology and Applications*, 2nd ed., John Wiley & Sons, Chichester, West Sussex, England, 2004.

[2] Koenigsberg, D., *"Water Warriors," UCLA Magazine*, www.magazine.ucla.edu/features/waterwarriors, July 1, 2006.

[3] Cadotte, J., King, R.S., Majerle, R.J., Peterson, R.J., "*Interfacial Synthesis in the Preparation of Reverse Osmosis Membranes,*" *Journal of Macromolecular Science and Chemistry*, A15, 1981.

These membrane-based separation technologies are categorized here by the nature of the driving force for separation, in this case either pressure or electrochemical.

Pressure-Driven Membrane Separation Technologies: Microfiltration, Ultrafiltration, Nanofiltration, Reverse Osmosis

Pressure-driven membrane separation technologies rely on a difference in pressure, from the feed side of the membrane to the permeate side, which forces water through the membrane. In this manner, water can be recovered from solutions containing both suspended and dissolved solids. MF, UF, NF, and RO are the primary pressure-driven membrane technologies. MF and UF deal with removing suspended solids from the solution, while NF and RO remove dissolved solids. Figure 8.1 shows a filtration spectrum that compares removal capabilities for several types of pressure-driven membrane and conventional filtration techniques.

Filtration

Pressure-driven membrane systems can operate in either dead-end or cross-flow filtration modes.

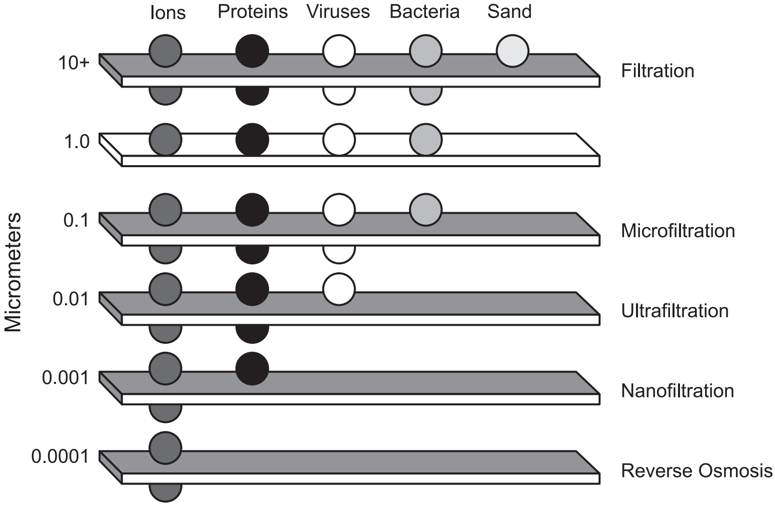

Figure 8.1 Removal capability of multimedia filtration and pressure-driven membrane technologies. (*Courtesy of Scrivener Publishing*.)

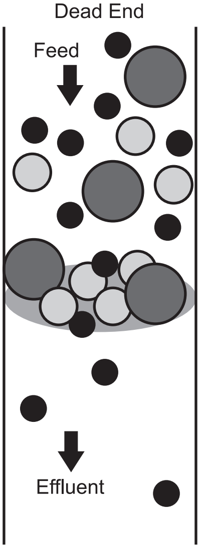

FIGURE 8.2 Principle of dead-end filtration.

Dead-End Filtration

Picture a filtration medium, such as a coffee filter, that allows a fluid (water) and some solids (coffee grounds) to pass through but retains the bulk of the coffee grounds.

As shown in Fig. 8.2 dead-end filtration operates with one feed stream and one effluent stream; is it well suited for batch-type operations. In dead end filtration, solids accumulate on the membrane surface relatively quickly, requiring frequent cleaning of the membrane to remove the foulants. Dead-end systems commonly used for MF and UF applications, are cleaned using three techniques: online backwashing, chemical-enhanced backwashing (CEB), and clean-in-place (CIP). Online backwashing involves intermittent backwash with filtered water plus an air pulse to help lift solids off the membrane. Backwashing can occur once every 15 to 60 minutes, depending on the concentration of solids in feedwater (higher concentration results in more frequent backwashing). A CEB using acid or caustic plus hypochlorite is performed occasionally along with the backwash step to remove inorganics (low pH) and organics and biofouling (high pH and chlorine). CIP is performed every few months as needed to remove materials from the membrane that backwashing and CEB do not. (See the section on cleaning for more details about CEB and CIP.) Many, if not most, MF and UF systems operate in dead-end mode.

Cross-Flow Filtration

In cross-flow filtration, feedwater flows tangentially across the surface of the membrane and not all water sent to the membrane actually permeates it. Hence, cross-flow filtration has one influent stream but two

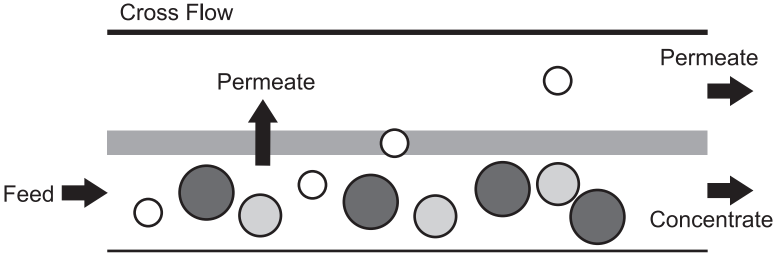

FIGURE 8.3 Principle of cross-flow filtration.

effluent streams (versus a single effluent stream for dead-end filtration). The rationale behind cross-flow filtration is that fluid traveling tangentially to the membrane surface essentially scours the membrane surface free of solids that might foul the membrane. Hence, cross-flow filtration is, in theory, a continuous operation, rather than a batch process. In practice, however, the membrane will become fouled enough with time to warrant an occasional cleaning to remove solids from the membrane. Figure 8.3 depicts a cross-flow pattern across a membrane. Virtually all RO/NF systems operate in cross flow. Some MF and UF systems with their feed on the inside of a hollow fiber membrane, also exhibit characteristic cross flow across the membrane, but are usually operated in an overall dead-end mode. Alternately, some MF and UF systems with inside-out feed operate in true cross flow, with the recycle of concentrate back to the front of the system, for streams with consistently high concentrations of suspended solids.

A phenomenon that occurs with cross-flow filtration is concentration polarization; this phenomenon is most pronounced with plate-and-frame, tubular, and spiral wound membrane modules. It involves increased fouling in the diffusion boundary layer next to the membrane surface, and is exacerbated by low cross-flow velocity and high water flux through the membrane. Concentration polarization is discussed in more detail later in this chapter.

Basic Membrane Terminology

Recovery

Recovery is defined as the amount of feedwater that passes through the membrane to become "permeate." It is expressed in terms of percent of feedwater that becomes permeate [Eq. (8.1)].

$$\text{Recovery (\%)} = \left(\frac{\text{Permeate Flow}}{\text{Feed Flow}}\right)(100) \tag{8.1}$$

The higher the recovery of the system, the lower the amount of wastewater generated. Recovery generally ranges from about 50% to as high as 90%, depending on the application. The most common recovery is 75% for most industrial and commercial applications. Recovery is set by the RO system designer and is a balance between the amount of wastewater generated and the degree to which feedwater becomes concentrated as more water is recovered as permeate.

Rejection

Rejection (or salt rejection) is generally a term applied to RO and NF processes. It is defined as the degree to which a given species is retained by the membrane. It is expressed in terms of percent of feed concentration [Eq. (8.2)].

$$\text{Rejection (\%)} = \frac{[(\text{Feed Concentration}) - (\text{Permeate Concentration})]}{(\text{Feed Concentration})}(100) \tag{8.2}$$

The higher the rejection, the more concentrated the permeate *and* concentrate streams become. Rejection is typically dependent on the specific species and the specific membrane. Rejection is a property of the membrane; it is not set by the designer of the RO/NF system. Salt passage is opposite of rejection. A 98% rejection rate corresponds to 2% passage through the membrane of the solute in question.

Concentration Factor

Concentration factor is a term that is again used primarily with RO and NF processes. It is used to determine the relative concentration of the concentrate stream to the feed stream. Concentration factor is calculated by taking the feed flow rate and dividing it by the concentrate flow rate [Eq. (8.3)].

$$\text{Concentration Factor} = \text{Feed Flow}/\text{Concentrate Flow} \tag{8.3}$$

This factor is then used to multiply the feed concentration to determine the approximate concentrate concentration of a species of interest, in a manner similar to cycles of concentration in a cooling tower.

Flux

Water flux is the amount of water that passes through a given membrane area during a given unit of time [Eq. (8.4)]:

$$J_w = A\ (\Delta P - \Delta\pi) \tag{8.4}$$

where J_w = flux of water
A = water permeability coefficient [partition coefficient for water * (diffusivity of water/membrane thickness)]
ΔP = ln mean average of applied driving pressure
$\Delta\pi$ = ln mean average of osmotic pressure

Water flux is expressed in gallons per square foot per day (gfd), liters per square meter per hour (lmh), or cubic meters per square meter per day (M/d).

Water flux is an important design variable, as this flux rate can have a direct impact on the degree and rate of fouling and scaling of the membrane. Flux is a direct measure of the rate at which material is transported to the surface of the membrane. Material that does not pass through the membrane is then trapped in the concentration polarization boundary layer, where the slow rate of diffusion away from the membrane gives solutes and scale sufficient time to foul and scale the membrane (see the following discussion on concentration polarization). The lower the feedwater quality, the greater the potential for fouling and scaling the membrane as water flux increases.

Salt flux is the amount of a solute that passes through a given membrane area during a given unit of time [Eq. (8.5)]:

$$J_S = B\,(C_{A2} - C_{A3}) \tag{8.5}$$

where J_s = flux of solute
B = salt permeability coefficient [partition coefficient for salt * (diffusivity of salt/membrane thickness)]
C_A = mass concentration of solute A
subscripts:
2 = in the membrane boundary layer
3 = in the permeate

Salt flux is expressed in terms of mass per membranes area per unit time [e.g., grams per square meter per hour (g/m^{2}h)].

Concentration Polarization

Concentration polarization is a phenomenon that occurs in boundary layer next to a surface that forms whenever there is fluid flowing across the surface (Fig. 8.4). Within most membrane modules, the bulk solution experiences turbulent, convective flow, while very near the membrane surface, there is little to no convective flow. Diffusion is then, the primary transport mechanism of material to and from the membrane surface. Diffusion is slower than convection, so there is a

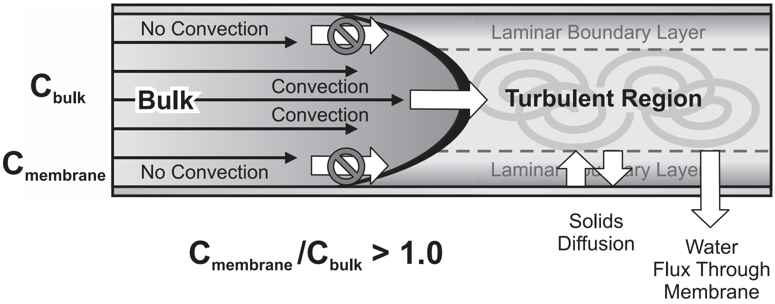

Figure 8.4 Boundary layer in cross-flow filtration. (*Courtesy of Scrivener Publishing*.)

tendency for build-up of solids (both suspended and dissolved) in the boundary layer, and hence, on the surface of the membrane. This build up is exacerbated by the flux of water and solids toward the membrane, and when the water flows through, most of the solids are retained on the membrane; higher water flux leads to more rapid buildup of solids on the membrane. This build up leads to membrane fouling and scaling, if the suspended and dissolved solids are given enough residence time to remain in the boundary layer (the residence time is a function of the boundary layer thickness).

Boundary layer thickness is a function of bulk solution velocity along the membrane surface, with higher velocity resulting in a thinner boundary layer. Thinner boundary layer reduces the tendency for the membrane to foul or scale, as the residence time for solids in the layer is reduced as compared to a thicker boundary layer.

Water flux through the membrane also impacts the degree of concentration polarization. Flux brings even more solids into the boundary layer and to the membrane surface. Since the bulk of these solids do no pass through the membrane, but the water does pass, the concentration becomes even higher in the boundary layer. Hence, higher water flux leads to higher concentrations of solids in the membrane boundary layer, increasing the tendency to foul and scale the membrane.

Membrane Modules

Membranes are modularized for practical use. The objective is to pack a relatively large membrane area into a relatively small volume. There are five basic types of membrane modules, as described in Table 8.1.

Module Type	Packing Density (Approx. m^2/m^3)	Ability to Clean	Cost/ft^2
Flat sheet (plate-and-frame)	Moderate (150–500)	Moderate	Moderate to high
Tubular	Low (20–275)	Easy	Moderate
Spiral wound	Moderate to high (500–1250)	Difficult	Moderate
Hollow fiber	High (NA)	Moderate	Moderate to low
Hollow fine fiber	Very high (500–4950)	Difficult	Low

Table 8.1 Comparison of Five Basic Types of RO Membrane Modules[4]

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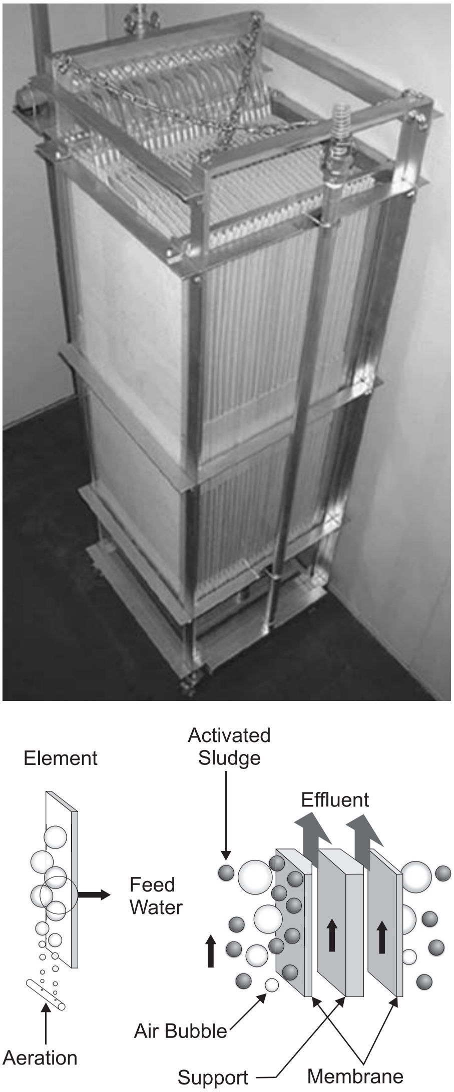
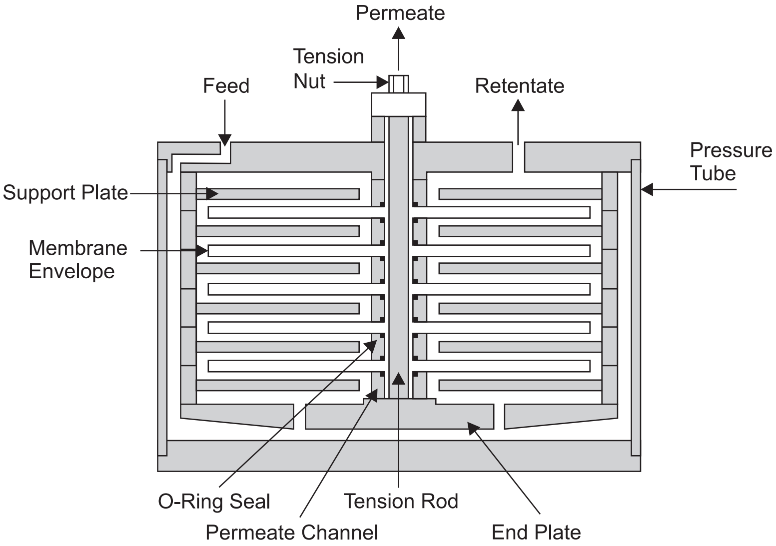
[4] Kucera, J., *Reverse Osmosis: Design, Processes, and Applications for Engineers*, 2nd ed., John Wiley & Sons/Scrivener Publishing, Beverly, MA, 2015.

Flat Sheet—Plate-and-Frame

Flat sheet and plate-and-frame membranes are generally used in membrane bioreactors (MBRs) and specialty, high-solids RO application, respectively. Plate-and-frame modules are also used in CEDI applications. Figures 8.5 and 8.6 show a flat-sheet arrangement for an MBR application, and an RO plate-and-frame module, respectively.



Figures 8.5 Flat-sheet membrane as used in a submerged MBR application. (*Courtesy of Toray Industries*.)



Figures 8.6 Plate-and-frame module for RO applications. (*Courtesy of Scrivener Publishing*.)

Tubular

Tubular membrane modules were the first commercially viable RO membranes used in 1965 at the first commercial brackish water RO application at the Raintree facility in Coalinga, California.[5] Today, tubular membranes are typically used for high suspended solids, and oil and grease removal using MF or UF. They are also used in external MBR applications and with ceramic membranes.

Some polymeric tubular modules resemble shell-and-tube heat exchangers. The feed is on the tube side and the permeate exits the module on the shell side. Inner diameters of the membrane tubes can vary from about 5 to 12.5 mm, or even larger, depending on the application. Several membrane tubes can be contained in a single metal, perfluorocarbon (PFC) or fiber-reinforced plastic (FRP) housing.

Some modules are easily cleaned using a sponge ball that is sent down the tube, wiping the surface of the membrane; this technique is generally used for larger diameter tubes. For smaller tubes, frequent cleaning (and backwashing for MF and UF modules) is recommended; cleaning may be as frequent as once a day for applications such as dairy processing.

Tubular modules may also contain several multibore fibers, as shown in Fig. 8.7. These fibers have capillary tubes with smaller diameters.

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[5] Ibid.

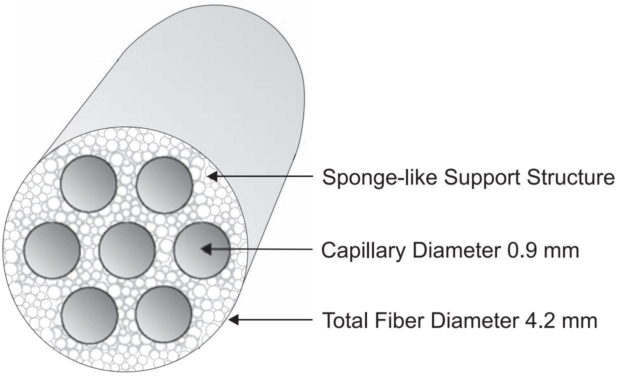

Figure 8.7 Multibore, polymeric tubular membrane.

Spiral Wound

Spiral wound modules are predominant for RO and NF applications, but this configuration has also been employed for MF and UF, as well as CEDI applications.

Figure 8.8 is a cross section of a spiral wound module. The module consists of sheets of membranes placed between feed and permeate spacers. Two membranes are placed back-to-back and separated by a spacer. This package is then glued on three sides, so that any permeate that goes through the membranes can only exit at one end of the permeate spacer. Several of these membrane packages or "leaves" are

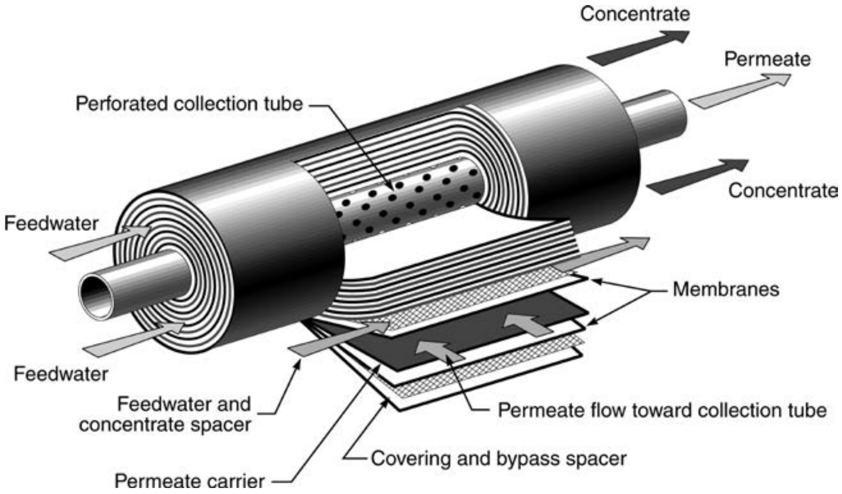

Figure 8.8 Spiral wound RO module cross section.

created and then wound around a perforated tube called the permeate tube. The open end of the membrane leaf is toward the permeate tube. Each leaf is separated by a feed channel spacer through which the feed/concentrate stream runs. Feedwater enters the end of the module and travels through the feed channel spacer along the surface of the membrane. Permeate is collected in the permeate spacers and spirals down into the permeate tube and exits the module. Concentrate exits the module at the opposite end to where feedwater enters.

The most common diameters of spiral wound modules are 2.5 inches (63.5 mm), 4 inches (102 mm), 8 inches (203 mm), and 16 inches (406 mm) with lengths of 40 inches (1 m) and 60 inches (1.5 m), and containing up to more than 1000 ft^2 (92.9 m^2) of membrane area.

Hollow Fine Fiber

Hollow fine fibers and modules were first commercially introduced by E.I. DuPont de Nemours and Company in 1970 with the DuPont B-9 (and, in 1974, the B-10) Permeator. The hollow fine fibers are similar to the hollow fibers described later, but are of different polymer composition (linear aromatic polyamide or "aramid") and are also much finer in construction. The fibers are as flexible as human hair (Fig. 8.9), but are finer. Despite their fine nature, the fibers are self-supporting, with a ratio of outside to inside diameter of at least 2 to 1 (Fig. 8.10), allowing these fibers to withstand pressures up to 69 bar (1000 psi).

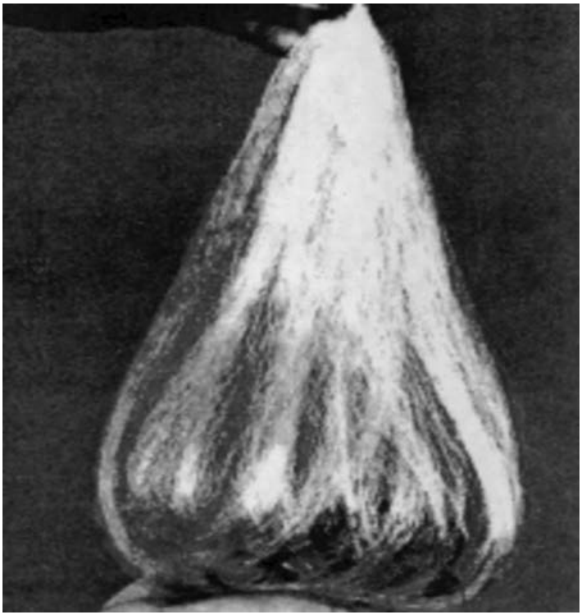

Figure 8.9 Hollow fine fibers.

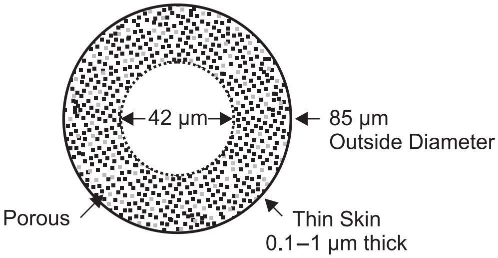

FIGURE 8.10 Cross section of a hollow fine fiber. (*Courtesy of Scrivener Publishing*.)

Hollow fine fiber modules are constructed using fibers that are mounted in a U-fashion in a pressure vessel; fibers are fixed in place with epoxy at both ends, as shown in Fig. 8.11. The configuration resembles a shell-and-tube exchanger, with feedwater entering the shell side of the pressure vessel and permeate exiting through the fiber lumens (known as "outside-in" flow). The DuPont B-9 Permeators could produce up to 94.6 M^3/d (25 000 GPD) for a 254 mm (10 inches) diameter module. The primary disadvantage of this configuration is that the fibers within the modules are prone to fouling with any solids in the feedwater, due to the tight packing of the fibers.

While DuPont no longer manufactures hollow fine fiber RO membranes and modules, hollow fine fiber modules can be found today, most notably the Hollosep membrane modules from Toyobo.

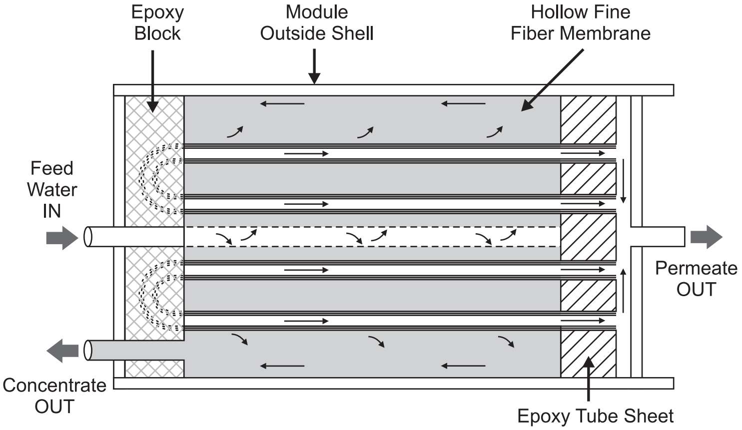

FIGURE 8.11 Hollow fine fiber module. (*Courtesy of Scrivener Publishing*.)

Figure 8.12 Hollow fiber membranes for MF and UF applications.

Hollow Fiber

Hollow fiber membranes are used primarily for MF and UF applications, although some have been used in research activities for RO.[6] These fibers differ from hollow fine fibers in that the diameter or the hollow fibers are many times larger than that for hollow fine fibers (Fig. 8.12). Hollow fibers used for UF applications can have an inside dimeter (ID) of up to 1 mm, fully 25 times larger than the ID of the DuPont Permasep hollow fine fiber, RO membranes[7] with a fiber wall thickness of 100 to 200 μm. For RO applications, these fibers can have IDs of 250 to 300 μm, roughly six times that of the DuPont Permasep hollow fine fibers.[8] Fiber wall thickness of 400 to 500 μm has been used for RO applications and did not require an external pressure vessel; the fibers themselves acted as the pressure vessels.[9]

Hollow fiber membranes can operate in outside-in flow or inside-out flow (inside fiber or "lumen" feed) (Fig. 8.13). Inside-out flow more closely resembles cross-flow filtration, in that all portions of the inside surface (feed side) is continuously scoured by the flow of fluid across it, thereby minimizing fouling of the membrane surface. For outside-in flow, the fibers are typically scoured with air bubbles (Fig. 8.14) to try to minimize collection of solids on the outside (feed)

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[6] Ray, R.J., Babcock, W.C., Barss, R.P., Andrews, T.A., LaChapelle, E.D., SAE Technical Paper Series 840933, 1984.
Baker, R.W., Barss, R.P., assigned to USA US Patent 4,772,391, 1988.

[7] Porter, M.C., "Ultrafiltration," in *Handbook of Industrial Membrane Technology*, M.C. Porter ed., William Andrew Publishing/Noyes, Norwich, NY, 1990.

[8] Ray, R.J., Babcock, W.C., Barss, R.P., Andrews, T.A., LaChapelle, E.D., SAE Technical Paper Series 840933, 1984.
Baker, R.W., Barss, R.P., assigned to USA US Patent 4,772,391, 1988.

[9] Baker, R.W., Barss, R.P., assigned to USA US Patent 4,772,391, 1988.
Ray, R.J., Kucera-Gienger, J., Retzlaff, S., *Journal of Membrane Science*, 28:1986.

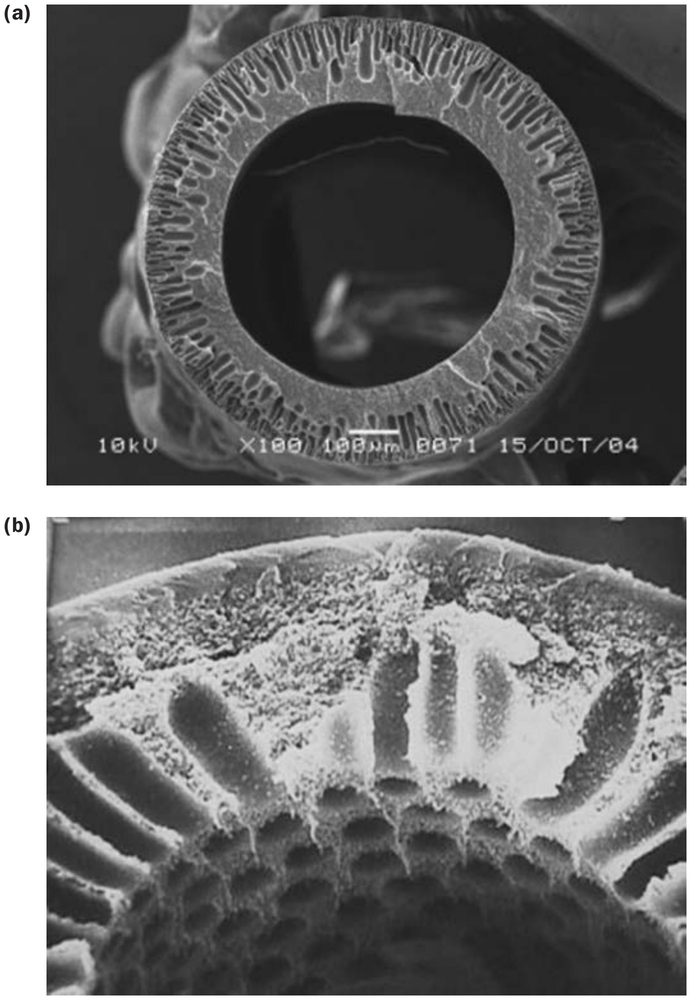

Figure 8.13 Cross section of an inside-out feed ("inside skinned") (a) and outside-in feed ("outside skinned") (b) hollow fiber membranes.

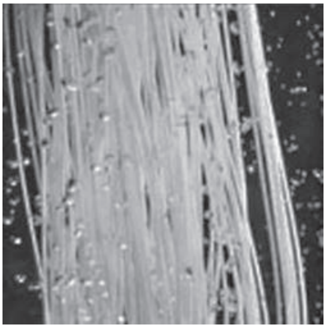

Figure 8.14 Air scour of submerged hollow fiber membranes.

of the fibers when used in submerged MF or UF applications, as discussed earlier.

Hollow fiber membranes for MF and UF applications are either modularized into cylindrical canisters or cassette (for submerged processes), as shown in Figs. 8.15 and 8.16, respectively. Since the operating pressure of MF and UF applications is less than about 3.5 bar (50 psi) for most pressurized hollow fiber applications, and less than a vacuum 1 bar, the modules do not require pressure vessels. Unlike the hollow fine fiber configuration with the U-shaped

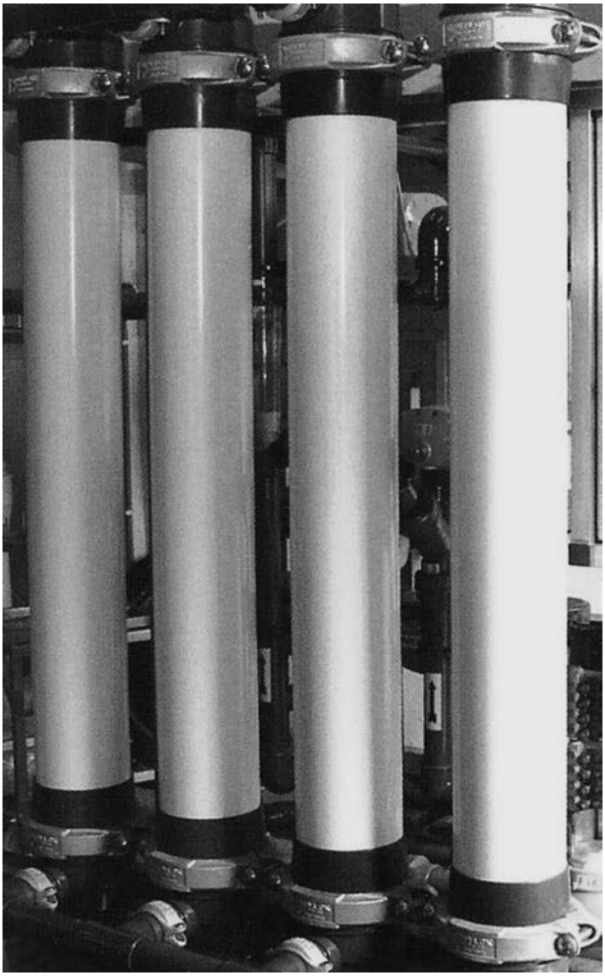

Figure 8.15 Canister-type hollow fiber membrane modules for MF and UF applications.

Figure 8.16 Cassette-type hollow fiber membrane modules for submerged MF and UF applications.

fiber bend, which are potted and open at only one end, (as shown in Fig. 8.11), most hollow fiber membranes are potted and open at both ends (the exception is the Koch Puron® submerged fibers, which are potted only at the bottom of the cassette).

Microfiltration and Ultrafiltration

Introduction

MF and UF are similar, pressure-driven membrane separation techniques used to separate suspended solids from solution. These membranes have pores, through which the carrier fluid (typically water) and some solids pass. Separation of solids from solution by the membrane is based on size exclusion, where particles larger than the pore size of the membrane are retained, while smaller particles pass through into the permeate. Note that in many cases, solutes can adsorb onto the surface of a pore, thereby reducing pore size and enhancing ability of the membrane system to reject particles smaller than the pore size rating. This phenomenon also contributes to an increase in pressure across the membrane, known as transmembrane pressure (TMP—the pressure from the feed side to the permeate side of the membrane). Transmembrane pressure is a function of the degree of fouling of the membrane surface as well as within the pores. The higher the TMP, the lower the driving force and efficiency of the MF process. Once the TMP reaches a predetermined value, for example, 150 kPag, (22 psig) the membranes must be cleaned (or replaced if unable to clean sufficiently) to restore efficiency.

Membranes

Most MF and UF membranes are made from the same synthetic organic polymers, but are prepared under different conditions to produce different pore sizes. Pore sizes for MF membranes average around 0.1 μm, while UF membrane pore sizes are on the order of 0.02 to 0.03 μm. Typical MF and UF polymers include polyvinylidine fluoride (PVDF), polysulfone (PS), polypropylene (PP), and polyacrylonitrile (PAN). Additionally, polyethersulfone (PES) is used for UF membranes, and polytetrafluoroethylene (PTFE), nylons, cellulose triacetate, and cellulose acetate-cellulose nitrate blends are used for MF membranes.

High strength and good elongation characteristics are important for the integrity of the MF or UF membrane, particularly in the hollow fiber format. Hollow fiber membranes, whether pressurized or submerged, tend to move in the turbulence of the feedwater flow, so the ability of the fiber to flex without breaking is a necessary trait.

Hydrophilicity is also a membrane characteristic of importance. Hydrophilic membranes tend to adsorb water more readily than hydrophobic membranes. Table 8.2 lists the surface tension for some

Polymer	Surface Tension (dynes/cm)
Polytetrafluoroethylene	18
Polyvinylidene fluroide	25
Polypropylene	29
Polysulfone	41
Polyacrylonitrile	44
Cellulose	44

Table 8.2 Surface Tension of Various MF and UF Polymers

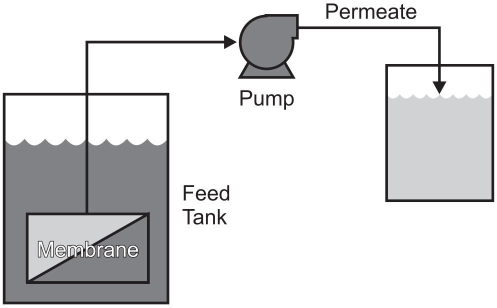

Figure 8.17 Submerged MF/UF process.

polymeric materials used for MF and UF membranes; the higher the surface tension, the more hydrophilic the material. Hydrophilic membranes are more wettable and require lower operating pressure than hydrophobic membranes. Additionally, since potential foulants in water tend to be hydrophobic, a hydrophilic membrane prefers to bind to water rather than the foulant.

Modules

While MF and UF membranes are modularized into several different configurations, including flat-sheet, spiral wound, and tubular, the most common configuration is the hollow fiber or "capillary." Hollow fiber modules can be used in submerged applications (such as MBR) and pressurized applications. Figures 8.17 and 8.18 depict submerged and pressurized processes, respectively. In the submerged process, the membranes are submerged in a tank containing the feed solution, and a vacuum is pulled on the lumen side of the fiber to pull through relatively clean permeate. Submerged processes are outside-in flow only. In the pressurized process, the feed solution is pressurized which forces permeate through the membrane. The pressurized process can be outside-in or inside-out flow.

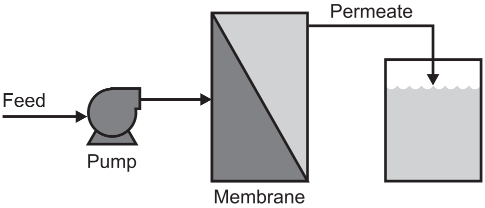

Figure 8.18 Pressurized MF/UF process.

Parameter	Units	Nominal	Maximum
Particle size	μm	<150	300
Turbidity	NTU	<50	300
Total suspended solids	mg/L		100
Total organic carbon	mg/L	<10	40
Oil and grease	mg/L	0	<2

Table 8.3 General Feedwater Quality Guidelines for MF and UF Hollow Fiber Systems

Pretreatment

Pretreatment for MF and UF systems is relatively straight forward. Table 8.3 lists generalized feedwater limits for most hollow fiber systems.

Pretreatment usually includes a screen filter rated at 100 to 300 μm, to keep large particles out of the membrane modules. In some cases, clarification is also required if the feedwater routinely exceeds the feedwater quality guidelines.

Cleaning

Submerged Hollow Fibers Submerged hollow fiber membranes typically employ a full-time air scour during operations in order to keep membranes clean. Most hollow fiber membranes are potted at both ends of the module (some are only potted at the lower end, as mentioned earlier). Solids tend to accumulate near the potted end(s) since the fibers don't have as much room to move to allow the air to scour the fibers clean.

A back pulse of permeate, from the inside to the outside of the fibers for submerged systems, is used in an attempt to dislodge solids from the feed surface of the membrane fiber. Sometimes, acid, caustic, or chlorine is added to the back pulse to further clean the membrane fiber. Pure water back pulses can occur every 15 to 30 minutes with a duration of 10 to 30 seconds.

Cleaning of submerged membranes involves either evacuating the tank containing the membrane modules and preparing the cleaning solution *in situ*, or removing the rack of modules and placing them in another tank for cleaning. Removing the modules also allows for cleaning by spraying water directly onto the fiber bundles to remove solids.

Pressurized Hollow Fibers Cleaning of a pressurized, hollow fiber system involves several steps: backwash, CEB, and CIP.

Backwash Backwashing is conducted once every 15 to 90 minutes, depending on the degree of membrane fouling that occurs. Backwashing involves sending permeate back through the membrane to the feed side, in an effort to remove solids that have be collected on the feed-side membrane surface. Air scour is sometimes used to assist in sweeping away solids that have been dislodged from the membrane by the backwash. A forward flush to drain is then used to ensure that solids removed during backwash and air scour, are removed from the system prior to bringing the unit back on line. Total backwash/flush time can range from about 90 to 180 seconds.

Chemical Enhanced Backwash A chemical enhanced backwash is a "mini clean," where chemicals are added during the backwash cycle to assist in removing inorganics (such as scale), organics, and bacteria from the membranes. Chemicals used during a CEB include:

- Citric or hydrochloric acid (HCl), for inorganic scale and iron removal; sample concentrations include up to 1000 mg/L of 35% HCl
- Caustic (NaOH) at concentrations up to 500 mg/L of 50% NaOH is used for removal of organic fouling
- Hypochlorite (NaHOCl) at concentrations up to 1000 mg/L is used for biogrowth control.

Frequency of CEB depends on the specific water being processed; caustic and hypochlorite are typically feed together and can be used as often as once every 2 to 12 hours, while acid is generally used less frequently, perhaps once every 12 to 72 hours. Total duration of a CEB is approximately 3 to 5 minutes.

Clean-in-Place A CIP is performed when the backwashes and CEBs can no longer maintain flux or TMP. Chemicals used and concentrations are shown in Table 8.4. A typical CIP requires 2 to 2.5 hours to complete.

Chemical	**Hydrochloric Acid HCl**	**Sodium Hydroxide NaOH***	**Hypochlorite NaHOCl***
Addresses	Inorganics	Organics	Bacteria
Percent, %	35	50	10
Concentration, mg/L	2000	1000	2000
pH	2	12	12

---

*Typically used together.

Table 8.4 Clean-in-Place Chemicals Used for MF and UF Pressurized, Hollow Fiber Membranes

Monitoring

There are a few parameters that are monitored with MF and UF systems, including operating pressure, temperature, and flux (or permeability).

Perhaps the most important parameter to determine is transmembrane pressure (TMP) and temperature-corrected TMP (TCTMP). The TMP or TCTMP is a measure of the degree of membrane fouling, and is determined by the pressure difference between the feed side and the permeate side of the membrane. As the resistance to permeation of the fouling and membrane increases, the TMP must increase to maintain flux and/or the flux decreases [see Darcy's law, Eq. (8.6)]. Under constant pressure, some MF and UF membranes operating on particularly challenging waters can lose 50 to 75% of water flux between backwashes due to fouling and the increase in resistance to flow, R_t.

$$J = \mathrm{TMP}/\mu R_t \tag{8.6}$$

where J = flux

μ = viscosity of the solvent (e.g., water)

R_t = resistance of the membrane material + fouling, as a function of temperature

As the resistance to flow, R_t, increases due to fouling, the TMP must increase to maintain flux. At a maximum TMP [usually given by the specific membrane manufacturer, and ranges from 1.5 to 2.0 bar (22–30 psi)], the membranes are backwashed to restore performance. Figure 8.19 shows TMP as a function of time for a UF system operating on Detroit River water.

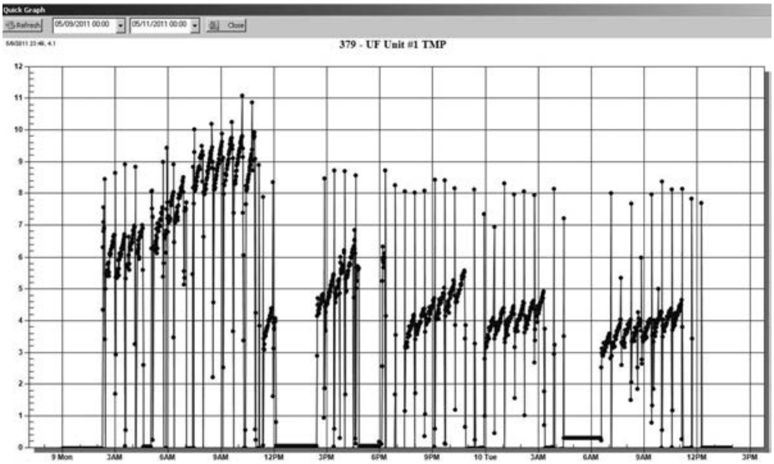

FIGURE 8.19 Transmembrane flux as a function of time for a UF system.

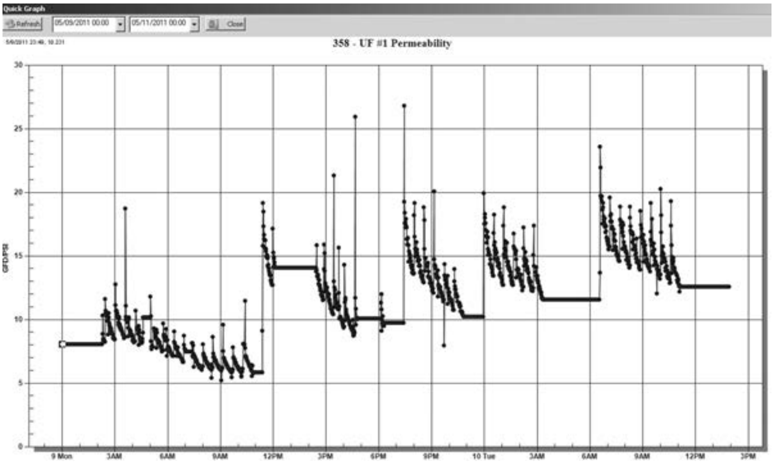

Figure 8.20 Permeability as a function of time for a UF system.

Performance is also measured in terms of permeability, which is productivity divided by feed pressure. Figure 8.20 shows the permeability as a function of time for the same system and time period as the TMP shown in Fig. 8.19. As fouling of the membrane and pressure increases, permeability of the system decreases.

Air integrity testing (AIT) is a test used to monitor the integrity of the membrane fibers for hollow fibers configurations. It is uncommon in industrial settings, but a requirement for municipal applications. The test involves pressurizing the feed side of the membrane modules with air at 1.2 to 1.4 bar (18–20 psi), while water is still on the permeate side of the fibers. The pressure should hold for 10 minutes. If the pressure decays during the 10 minutes, this is indicative of leaks in the modules, either through the fibers or around O-rings. If the system is built with clear piping for the permeate stream (Fig. 8.21), bubbles can be seen during the test if integrity is compromised. Fibers that are compromised will pass suspended solids into the system permeate stream, increasing the likelihood of fouling of any RO equipment downstream. Fibers can be removed from service by inserting a pin into the fiber of interest, as shown in Fig. 8.22.

Other parameters to monitor and trend directly from instrumentation:

- Conductivity—membrane feed
- Temperature—membrane feed
- Turbidity—membrane feed and permeate
- Pressure—membrane feed (both top and bottom of module is inside-out or cross flow feed) and permeate
- Flow—membrane permeate, backwash, waste, and recycle (if cross flow)

Figure 8.21 Ultrafiltration skid showing clear permeate piping.

Figure 8.22 Pinning broken fibers identified during air integrity testing.

Calculated performance data to trend include:

- Pressure—average feed side
- TMP and TCTMP
- Flux—permeate and backwash
- Specific flux and temperature-corrected specific flux—permeate flux divided by average feed side pressure

Microfiltration

MF is a pressure-driven membrane separation technique used for separating particles, including some bacteria, from liquid streams. As shown in Fig. 8.1, MF can remove particles about 0.1 μm in size. Specifically, MF membranes can be prepared with definite pore sizes, ranging from about 0.05 to 2 μm, such that particles of interest can be removed from solution by selecting the MF membrane with the proper pore size.

Microfilters are used to remove or reduce suspended solids, including turbidity and some algae and bacteria, from water (bacteria removal is 4-log, or 99.99%). As such, applications range from treatment of municipal drinking water to RO pretreatment of secondary and tertiary effluent and industrial systems. When MF is used for RO pretreatment, higher RO fluxes can be used, resulting in smaller RO systems to treat a given volume of feed (as shown in Table 8.9, higher RO flux rates can be used of feedwater treated with MF than with conventional pretreatment; higher flux means less membrane area is required to treat a given volume of water).

The use of MF for bioreactors has become very popular. MF membranes reduce the need for biomass sedimentation, allowing for smaller treatment tanks. MBRs can be used to treat wastewater for surface water discharge, urban reuse, groundwater recharge, industrial reuse, and irrigation.

Ultrafiltration

UF is a pressure-driven membrane separation technique used for separating particles such as colloidal silica and some higher-molecular weight soluble species, such as organics, from solution. UF relies on size exclusion, where species larger than the pore size or the molecular weight cut off (MWCO) are retained by the membrane, and smaller species pass through. Molecular weight cut off is a measure of the pore size of the membrane, from 0.1 to 0.001 μm for UF, in that it describes the ability of a UF membrane to retain 90% of a challenge macrosolute (typically polyethylene glycol, dextran, or protein).However, it should be noted that there is no international standard for MWCO, and MWCO ratings for membranes from different manufacturers cannot be directly compared. Molecular weight cut off does not refer to 100% retention because other factors, such as the shape of the species (spherical, linear, etc.) and operating conditions, contribute to the ability of the membrane to retain a specific species. In general, however, the pore size of a UF membrane is approximately an order of magnitude smaller than an MF membrane pore size. In contrast to MF, UF membrane can claim 6-log (99.9999%) removal of bacteria, and some jurisdictions allow for 4-log (99.99%) reduction of viruses with UF.

UF is used for a wide variety of applications, including concentration of proteins, recovery of electrodeposition paint, purification of bottled water, treatment of oily wastes, purification of blood, and RO pretreatment. When UF is used for RO pretreatment, higher RO fluxes can be used, resulting in smaller RO systems to treat a given volume of feed.

Reverse Osmosis and Nanofiltration

RO and NF are similar, pressure-driven membrane separation techniques used to separate dissolved solids from solution. RO and NF are used for a wide variety of applications, from seawater desalting for drinking water and electric power generation to makeup pretreatment for boilers and cooling tower systems. Typical uses include replacing sodium softening to increase boiler cycles in steam production, and replacing traditional cation/anion ion exchange to eliminate the need to store and handle acid, caustic, and regeneration waste.

Both RO and NF rely on a combination of charge exclusion and solution/diffusion permeation to affect separation (NF membranes also rely on size exclusion via pore structures, as discussed earlier). The solution/diffusion model (nonporous model) of transport through a membrane involves three important steps:[10]

1. Sorption of solute into the membrane
2. Diffusion of solute through the membrane
3. Desorption of solute out of the membrane

The solution/diffusion, or nonporous model of membrane transport assumes an ideal, defect-free, nonporous membrane. Although developed in the 1960s, it is still a valid transport model that is empirically well-approximated.

The ability of a solute to essentially dissolve and diffuse through a membrane polymer is a function of several variables, including temperature, pressure, concentration of solute, and membrane polymer

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[10] Lonsdale, H.K., Merten, U., Riley, R.L., "*Transport Properties of Cellulose Acetate Membranes*," *Journal of Applied Polymer Science*, 9, 1965.
Lonsdale, H.K., "*Recent Advances in Reverse Osmosis Membranes*," *Desalination*, 13:3, 1973.

selected. For example, NF membranes, by design, are created to pass more salts than RO membranes. NF membranes typically reject only up to about 75% of sodium chloride (although the range of rejection for various membranes is quite broad), while RO membranes typically reject more than 96%.

Ionic charge, polarity, and size of an ion play roles in the ability of an RO or NF membrane to reject or pass the ion. In general, NF and RO membranes are negatively charged. Negatively charged ions are repulsed (rejected) by the Donnan effect. This leads to the rejection of positively charged ions to maintain electrical neutrality in both the feed and permeate streams. The higher the valance, the greater the repulsion forces.[11] For example, the passage of sodium (+1 charge) is about double that of calcium (+2 charge) for a typical RO membrane, with passages of about 4% and 2%, respectively (rejections of 96% and 98%, respectively). The presence of polar functional groups within the membrane polymer serves to favor solubility of polar compounds, such as water, over nonpolar compounds, thus enhancing the flux of polar species over nonpolar species.[12] Larger species would be less soluble and also exhibit lower diffusivities through the membrane, essentially leading to high rejections of these species.[13]

Table 8.5 lists typical rejection for various species as functions of charge for two common RO membrane types, as well as the range of rejection for NF membranes. As the table shows, rejection of all species is higher for RO membranes than for NF membranes. This is by design, as NF membranes, also called softening membranes, are used primarily to reduce hardness from feedwater sources. NF membranes are often used in place of sodium softening to produce drinking water or boiler feedwater for low to medium pressure steam systems. Gases permeate very well through both NF and RO membranes because they are uncharged, polar, and small.[14]

Species	RO Membranes	NF Membranes
Divalent ions (Ca, Mg)	98–99%	90–98%
Monovalent ions (Na, Cl)	96–99%	50–95%
Gases (O_2, Cl_2, CO_2)	0%	0%

Table 8.5 Rejection of Various Species by RO and NF Membranes

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[11] Howe, K.J., Hand, D.W., Crittenden, J.C., Trussell, R.R., Tchobanoglous, G., *Principles of Water Treatment*, John Wiley & Sons, Hoboken, NJ., 2012.

[12] Howe, K.J., Hand, D.W., Crittenden, J.C., Trussell, R.R., Tchobanoglous, G., *Principles of Water Treatment*, John Wiley & Sons, Hoboken, NJ., 2012.

[13] Howe, K.J., Hand, D.W., Crittenden, J.C., Trussell, R.R., Tchobanoglous, G., *Principles of Water Treatment*, John Wiley & Sons, Hoboken, NJ., 2012.

[14] Howe, K.J., Hand, D.W., Crittenden, J.C., Trussell, R.R., Tchobanoglous, G., *Principles of Water Treatment*, John Wiley & Sons, Hoboken, NJ., 2012.

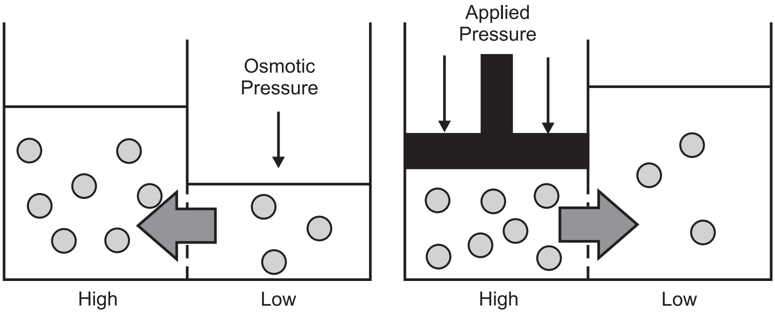

Figure 8.23 Concept of osmosis and reverse osmosis.

Osmosis and Reverse Osmosis

Osmosis should be understood first, in order to understand the basic principal behind RO and NF. Consider Fig. 8.23, where a container is separated into two compartments by a semipermeable membrane. This membrane allows water and some dissolved solids to pass through, but retains the majority of dissolved solids. One compartment has a relatively high concentration of dissolved solids, while the other compartment has a relatively low concentration of dissolved solids. Osmosis is the natural process by which water diffuses from the low concentration compartment, through the membrane, and into the high concentration compartment, in essence diluting the one solution. Water continues to diffuse in this direction until equilibrium is achieved, when the concentration of dissolved solids is the same in both compartments.

At equilibrium, there is a difference in height between the two compartments, and the difference corresponds to the osmotic pressure of the solution. The higher the concentration of dissolved solids, the greater the difference in height, and the greater the osmotic pressure of the solution. Approximately 4 kPa (0.6–1.1 psi) corresponds to 100 mg/L total dissolved solids (TDS). Therefore, for seawater at a concentration of 35 000 mg/L TDS, osmotic pressure is roughly 2.4 MPa (~350 psi). For brackish water with a concentration of about 1500 mg/L TDS, osmotic pressure is roughly 103 kPa (~15 psi).

If pressure is applied to the compartment containing that originally contained the higher concentration of dissolved solids, and that pressure is greater than the osmotic pressure of the solution, water is forced to move in the reverse direction. Water moves from the compartment being pressurized to the other compartment, leaving behind a more concentrated solution in the pressurized compartment, while generating relatively pure water in the other. This is RO.

While the description above depicts a batch, dead-end process, RO and NF systems rely on cross-flow filtration to affect separation of solutes from liquid. Figure 8.24 shows simplistically, how NF and RO systems functions. The concentration control valve is the key to operating

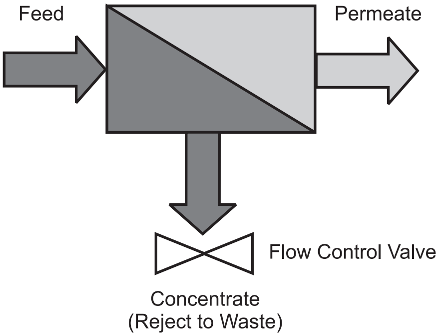

FIGURE 8.24 Conventional depiction of NF and RO operations.

the system, in that this valve is used to set the operating pressure and recovery of the system. Without this valve, RO and NF would be simply flow through the concentrate side of the membrane, with no resistance in terms of backpressure to force water from the high concentration feed, through the membrane, to the low concentration permeate.

RO and NF Membrane Materials

The most common RO membranes are either homogeneous, asymmetric cellulose acetate (CA) or a version of polyamide (PA) composite. Cellulose acetate membranes were the first commercially viable RO membranes developed and are still used today for some highly fouling and niche applications. These membranes consist entirely of the cellulosic material. Polyamide composite membranes, on the other hand, consist of a thin skin (typically 0.2 μm thick) of polyamide that is interfacially polymerized on top of a polysulfone support. The composite of the polyamide thin film and polysulfone microporous support, is supported on a non-woven fabric backing that plays no role in the performance (rejection and flux) of the membrane. Figure 8.25 shows a cross section of a composite membrane. Because of the composite nature, PA membranes are sometimes referred to as thin-film composites (TFC®). (Note that all PA membranes are TFC®, but not all TFC® membranes are composed of polyamide.) PA membranes exhibit higher rejection of silica and other solutes than CA membranes, and therefore, are used for most industrial (medium to high pressure boiler feed) and high-purity applications. Cellulosic membranes are used in bottled water processes where high rejection is not as critical and chlorine tolerance is essential, as well as some other niche applications. Table 8.6 compares characteristics of CA and PA membranes.

RO and NF membranes are very similar in that most NF membranes are based on polyamide chemistry.[15] However, some manufacturers

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[15] Lonsdale, H.K., Merten, U., Riley, R.L., "*Transport Properties of Cellulose Acetate Membranes*," *Journal of Applied Polymer Science*, 9, 1965.

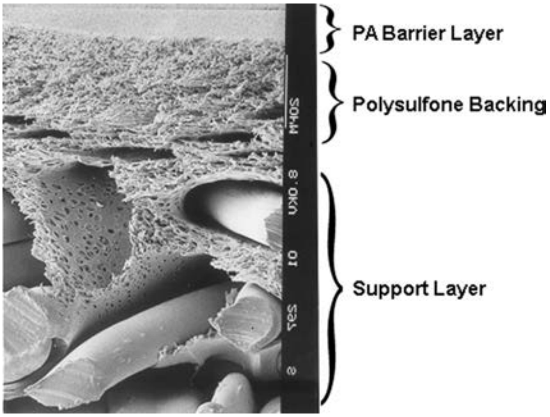

Figure 8.25 Composite membrane cross section.

use polypiperazine or polyethersulfone chemistries to adjust the performance of the membrane.[16] The performance of NF membranes spans a great range (Table 8.5), such that researchers have used the terms "loose" and "tight" to describe the various NF membranes. Tight NF membranes resemble low-pressure RO membranes in that the separation is based on the solution/diffusion model and charge exclusion, while loose NF membranes rely primarily on charge exclusion, and preferentially pass lower valence ions over ions with higher valence.[17]

Item	PA Membranes	CA Membranes
Membrane surface charge	Negative	Neutral
Membrane surface morphology	Rough	Smooth
pH range, continuous	3–10	4–6
pH range, cleaning	1–13*	3–7*
Operating pressure, psig (MPag)	150–400 (1–2.8)	200–600 (1.4–4.1)
Temperature, °F (°C)	113 (45)	95 (35)
Chlorine tolerance (continuous), mg/L	0 (<0.02)†	1.0

*Check with membrane supplier for actual limits
†Practical limit

Table 8.6 Comparison of PA and CA RO Membranes

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[16] Lonsdale, H.K., Merten, U., Riley, R.L., "*Transport Properties of Cellulose Acetate Membranes,*" *Journal of Applied Polymer Science*, 9, 1965.
[17] Bellona, C., "Nanofiltration—Theory and Application," in *Desalination: Water from Water*, J. Kucera ed., John Wiley & Sons/Scrivener Publishing, Beverly, MA, 2014.

There is debate in the membrane community whether RO and NF membranes have defined pore structures that contribute to mass transfer through the membrane.[18] While RO membrane performance can be described very well by the solution/diffusion model (nonporous model), NF can be adequately described by both porous (size exclusion) and nonporous modeling. Hence, most researchers now consider NF to span the gap between RO and UF membranes in terms of performance and mechanism of transport.

Modules

The first commercial RO membranes were tubular CA membranes installed in 1965 in Coalinga, CA. These membranes were easy to prepare. Figure 8.26 shows a schematic of the casting equipment used by Sidney Loeb in preparing these tubular membranes. But, the modules were more complicated to assemble. Figure 8.27 shows a cross section of a tubular RO module.

DuPont then developed the hollow fine fiber RO membranes and modules in 1967. While DuPont no longer makes RO membranes, some manufacturers (Toyobo) still make the hollow fine fiber membranes and modules.

Typical commercial RO/NF modules today are the spiral wound configuration. These modules are relatively easy to assemble using automated equipment. They can be manufactured in a wide range of sizes, with a broad range of membrane area per module, and various feed spacer thicknesses and configurations. For example, a standard 203 mm (8 inches) diameter, 1 m (40 inches) long module can contain anywhere from 32 to 41 m^2 (345–440 ft^2) of membrane area. The greater the membrane area per module, the thinner the feed spacer tends to be to allow for the additional membrane area. Feed spacer thicknesses for RO and NF applications range from about 28 to 34 mil. A thicker feed spacer provides a wider channel for feedwater, thereby reducing the tendency to foul the spacer, slowing the increase in feed-side pressure drop. This also allows for a more effective cleaning of the membrane. Research work has also improved the flow characteristics of feed spacers, to promote more turbulence in an effort to minimize concentration polarization and minimize “dead” zones on the membrane where fouling and scaling can occur.

Industrial spiral wound modules have an outer casing of fiberglass. There are also “sanitary,” or “full fit,” with a net that wraps around the module, without the outer casing. They are operated with a feed bypass to eliminate dead-zone hideouts for bacteria that

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[18] Bellona, C., “Nanofiltration—Theory and Application,” in *Desalination: Water from Water*, J. Kucera ed., John Wiley & Sons/Scrivener Publishing, Beverly, MA, 2014.

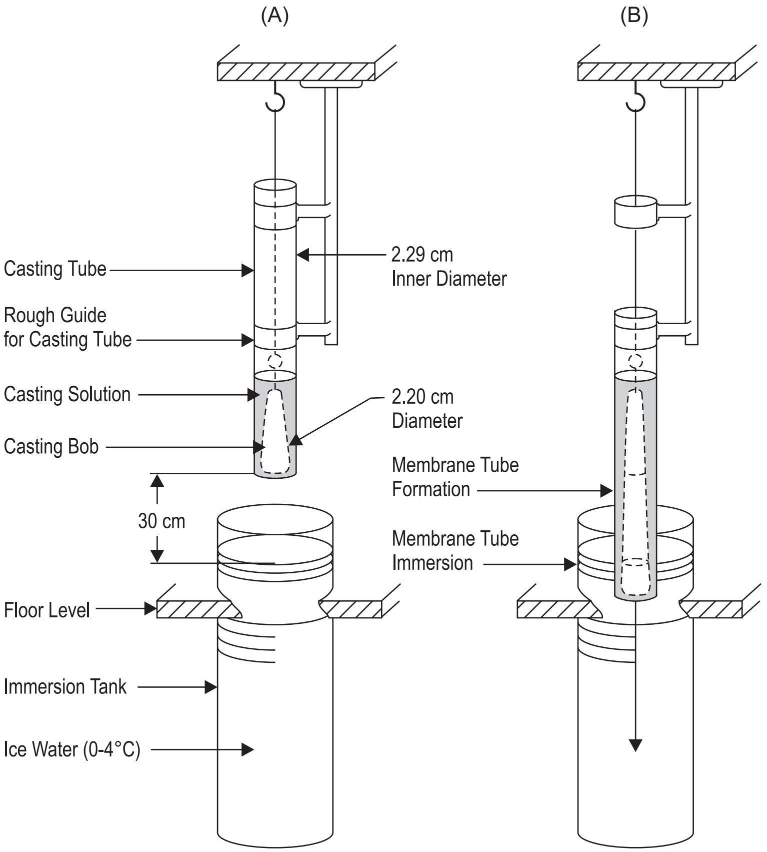

FIGURE 8.26 Schematic of tubular casting equipment used by Sidney Loeb to prepare the first commercially-viable RO membranes. (*Courtesy of Julius Glater, UCLA*.)

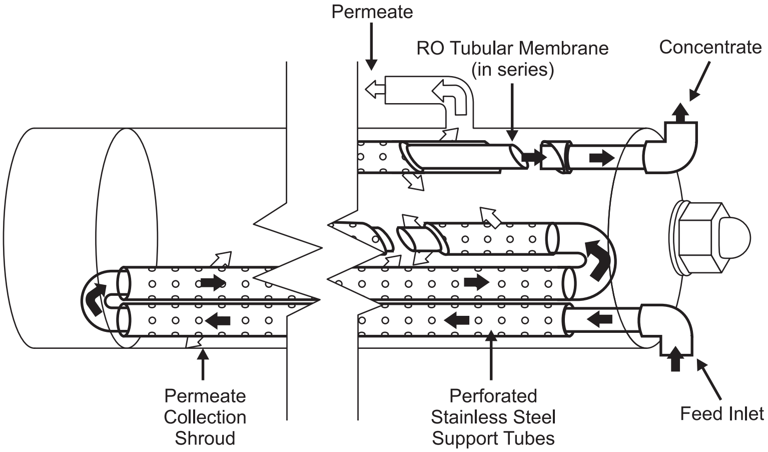

FIGURE 8.27 Tubular RO membrane module. (*Courtesy of Scrivener Publishing*.)

typically occur under the fiberglass casing. These modules are used in applications such as pharmaceuticals, and food and beverage, where hideout must be avoided.

High-temperature modules are available. These modules are typically full-fit, and are assembled using different materials, (e.g., glues) so that the membranes can be operated at higher temperatures. Some modules can be heat sanitized at up to 90°C (194°F), but must be chemically cleaned at 40°C (104°F) or below to prevent damage to the membrane itself. Pressure plays a role in how hot the modules can be operated, with higher pressure necessitating lower temperature. For example, some seawater membranes operating at 8.3 MPa (1200 psi) can only operate at 15°C (77°F) to minimize damage, while at 2.6 MPa (400 psi), a temperature of 70°C (158°F) is possible. Also, note that as the operating temperature increases, the rejection decreases, dropping to as low as 95% at temperatures greater than 70°C (158°F).

System Design

Figure 8.28 shows a typical cross-flow RO or NF configuration. This particular configuration is a 2:1 or "2 by 1" array. The first number in the array refers to the number of parallel pressure vessels and is called the first stage. The second number in the array refers to the number of parallel pressure vessels in what is known as the second stage. RO configurations may have just one, or as many as five or six stages.

Feedwater is divided more or less equally among pressure vessels in the first stage. The feed flows in a cross-flow manner across the surface of the membranes. Permeate from each membrane module in the first-stage pressure vessels is combined to become overall permeate from the first stage. Concentrate from each of the pressure vessels

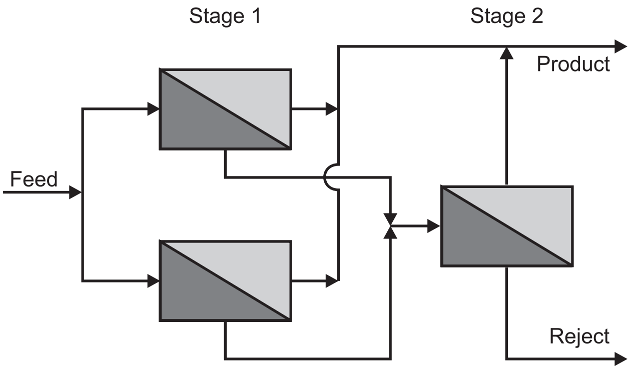

FIGURE 8.28 2:1 vessel array RO or NF system.

in the first stage is combined and becomes feed to the second stage. Permeate from each membrane modules in the second-stage pressure vessels is combined with the permeate from the first stage to become overall permeate from the system for this two-stage configuration. Concentrate from the second stage becomes overall concentrate from the system for a two-stage configuration. If there were a third stage, concentrate from the second stage would become feed to the third stage, and so on. The permeate from each successive stage is combined with the permeates from all the previous stages to become the overall permeate form the system.

The number of stages in an NF or RO system is determined by the overall recovery. In general, a stage containing six, 40-inches modules will recovery about 50% of the feedwater as permeate. Each additional stage serves to generate more total permeate from the system, resulting in less wastewater from the system. However, higher recovery means that the feedwater becomes more concentrated through each successive stage. And, as feedwater becomes more concentrated through each successive stage, the permeate also becomes successively more concentrated. Hence, higher recovery results in lower quality permeate. This is demonstrated for an RO system in Figure 8.29.

Figure 8.30 shows the flows and concentrations that would be expected given an RO system with 22.7 m^3/h (100 gpm) feed containing 100 mg/L TDS (this assumes the typical ~50% recovery per stage). Table 8.7 summarizes the conditions.

The number of pressure vessels in each stage is determined by velocity (typically measured using flow rate) through each pressure vessel. Table 8.8 lists the recommended concentrate flow rate

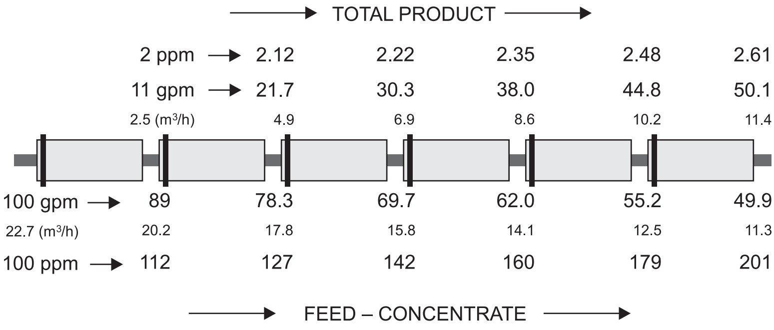

Figure 8.29 Water and mass balance through an RO pressure vessel illustrating the rising concentration of solids in both the feedwater and permeate as water is recovered (removed) from the feed. (*Courtesy of Scrivener Publishing.*)

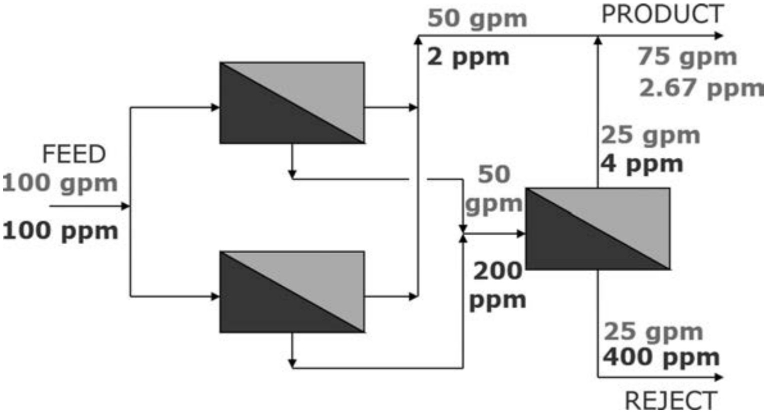

FIGURE 8.30 Water and ion balance in 2:1 RO array with 50% recovery per stage and 98% solute rejection.

out of a single pressure vessel as a function of feedwater quality for RO and NF systems. Since a higher velocity yields a thinner boundary layer and, hence, less concentration plarization, a high velocity is recommended for lower-quality feedwater, as shown in the table.

A third factor in determining the array for a given application is the overall water flux through the membranes. Table 8.9 lists the recommended water flux rates for feedwater as a function of the feedwater quality for RO and NF systems. Recall that higher flux leads to higher fouling and scaling due to concentration polarization effects. Hence, lower feedwater quality feed streams (e.g., higher concentration of suspended solids and scale forming minerals) require lower flux to minimize fouling and scaling, as

Location	Flow Rate, gpm (m^3/h)	Concentration, mg/L
Feed	100 (22.7)	100
Interstage permeate	50 (11.4)	2
Interstage concentrate	50 (11.4)	200
Second-stage permeate	25 (5.7)	4
Second-stage concentrate	25 (5.7)	400
Overall permeate	75 (17)	2.67

TABLE 8.7 Flow Rates and Concentrations through a 2:1 Array at 50% Recovery per Stage and 98% Solute Rejection

Feedwater Quality	365 ft^2 (33.9 m^2) Membrane Module, gpm (m^3/h)	400 ft^2 (37.2 m^2) Membrane Module, gpm (m^3/h)
RO permeate	10 (2.3)	10 (2.3)
Well water	13 (3.0)	13 (3.0)
Surface water, SDI* < 3	13 (3.0)	13 (3.0)
Surface water, SDI* < 5	15 (3.4)	15 (3.4)
Municipal wastewater, MF/UF pretreatment	16 (3.6)	18 (4.1)
Municipal wastewater, conventional pretreatment	18 (4.1)	20 (4.5)

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*Silt density index—see ASTM procedure D4189-07

Table 8.8 Recommended Minimum Concentrate Flow Rate versus Feedwater Quality for 8 Inches (203 mm) Diameter Spiral Wound Membrane Modules to Minimize Fouling and Scaling

Feedwater Quality	Recommended Flux, gfd* (L/[m^2•h])
RO permeate	21–25 (36–42)
Well water	16–20 (27–34)
Surface water, SDI† < 3	13–17 (22–29)
Surface water, SDI† < 5	12–16 (20–27)
Municipal wastewater, MF pretreatment	10–14 (17–24)
Municipal wastewater, conventional pretreatment	8–12 (14–20)

---

*Gallons per square foot per day

†Silt density index

Table 8.9 Recommended Flux versus Feedwater Quality to Minimize Membrane Fouling and Scaling Due to Concentration Polarization Effects

shown in Table 8.9. The advantage of higher flux rates is that less membrane area, hence smaller footprint and, more importantly, lower capital cost, are required.

Reverse Osmosis Permeate Polishing

For some applications, the permeate from an RO skid is not high enough to meet quality specifications. In these cases, RO permeate is

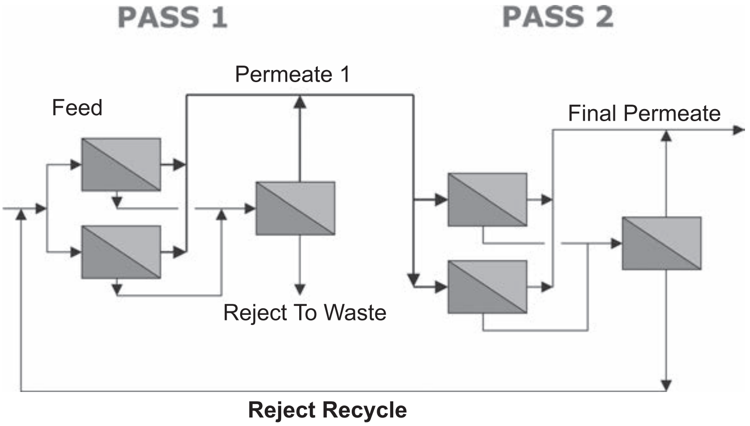

FIGURE 8.31 Two-pass RO system.

polished, typically using either mixed-bed ion exchange polishers, second-pass RO, or CEDI. The second-pass RO skid takes the permeate from the first-pass skid and further removes dissolved solids to reduce the concentration of species, such as silica. Figure 8.31 shows a two-pass RO system. Note that concentrate from the second-pass RO skid is virtually always recycled to the front of the first-pass RO skid. This is because quality of the second-pass concentrate is significantly better than feed to the first pass. This concentrate stream serves to dilute the system feedwater and to keep cross-flow velocity high. Both of these are measures that minimize fouling of first-pass membranes. Diluting the feedwater also improves overall permeate quality from the two-pass RO system.

Performance, Data Collection, and Analysis

The key to keeping an NF or RO system operating well is to measure the proper parameters and use appropriate analytical techniques to interpret the data. Table 8.10 lists data that should be collected from an NF or RO system at a minimum. Of these data points, perhaps interstage data are most critical, because these allow determination of where in the system performance has declined. For example, if pressure drop is higher over the first stage, one could surmise that issues that affect the first stage, such as fouling, are occurring. Likewise, decline over the second stage could imply membrane scaling. It should be noted, however, that many NF and RO skids do not come equipped with interstage monitoring capability, making troubleshooting more difficult. In these cases, other data, such as water quality and mass balances, are required to determine what issues are affecting the membranes.

	Feed	Interstage	Permeate	Concentrate
Pressure	X	X	X	X
Flow	X	*	X	
Conductivity	X	*	X	X
Temperature	X			
pH	X			*
Chlorine	X			

*Not necessary for non-critical applications.

Table 8.10 Minimum Data to Be Collected from an NF or RO System

Data Normalization Once data have been collected, it should be normalized to allow comparison with previous data and to allow trending. Comparison of actual data, such as permeate flow rates and rejection, is difficult because these parameters are functions of temperature, solute concentration, and pressure, as well as degree of membrane fouling, scaling, and degradation. Since these conditions vary constantly, it is virtually impossible to accurately compare data collected at different times. To address this issue, data is "normalized" or standardized to common temperature, pressure, and concentration, typically those at startup of new membranes (see ASTM D4516-00 for normalization calculations). Without the variables of temperature, pressure, and concentration affecting normalized permeate flow rate, changes in normalized permeate flow rate are due to membrane fouling, scaling, and degradation.

Normalized permeate flow is calculated using Eq. (8.7):

$$\text{Normalized Flow} = \frac{[(\text{AAP}_S - \Delta\Pi_S)]\text{TCF}_S}{[(\text{AAP}_a - \Delta\Pi_a)]\text{TCF}_a}(\text{Actual Flow}) \tag{8.7}$$

where AAP = the average applied transmembrane pressure

$$\text{AAP} = P_{\text{feed}} - \frac{\Delta P}{2} - P_{\text{perm}} \tag{8.7a}$$

where P_{feed} = applied feed pressure

ΔP = pressure *drop* from feed inlet to concentrate effluent

P_{perm} = permeate pressure

$\Delta\Pi$ = difference between the osmotic pressure on the membrane feed and permeate sides

TCF = temperature correction factor (membrane and manufacturer dependent)

Subscripts s = subscript for "standard" conditions
a = subscript for "actual" conditions

Figure 8.32 shows the slopes of normalized permeate flow curves for membrane degradation, fouling, and scaling, and no net change in normalized performance. Note that a flat curve may mean all is well with the system, or that membranes degradation and fouling/scaling are occurring simultaneously, and cancelling each other out. In this case, further investigative work is required to determine the status of the system.

Figures 8.33 and 8.34 show observed and normalized permeate flow rates for an actual RO system operating on a combination of Delaware River water and cooling tower blowdown. Figure 8.33 shows the observed permeate flow rate from this RO system. Operators did an excellent job of maintaining design productivity. However, in order to maintain the permeate flow rate of 77 M/h (340 gpm), operators had to gradually, but significantly, increase operating pressure of the system. Figure 8.34 shows normalized permeate flow rate for the same system. Normalized permeate flow rate does detect increased operating pressure to maintain productivity and reflects this as a decrease in normalized permeate flow.

Membranes in this example were periodically cleaned to restore performance. In addition, the pretreatment system to the membranes was upgraded to minimize membrane fouling that was occurring. As Fig. 8.34 shows, normalized permeate flow rate and observed permeate flow rate began to track at about day 90, indicating fouling issues were resolved.

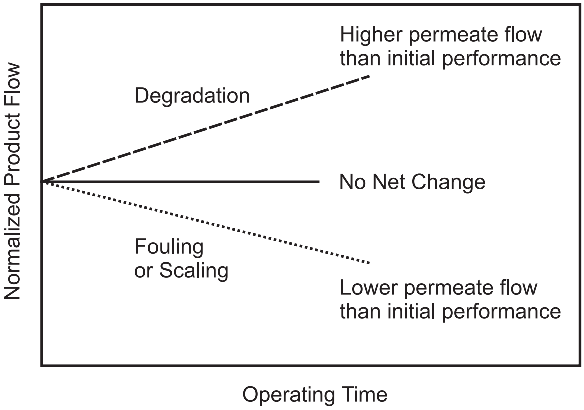

FIGURE 8.32 Normalized permeate flow slopes versus time and membrane fouling, scaling, and degradation.

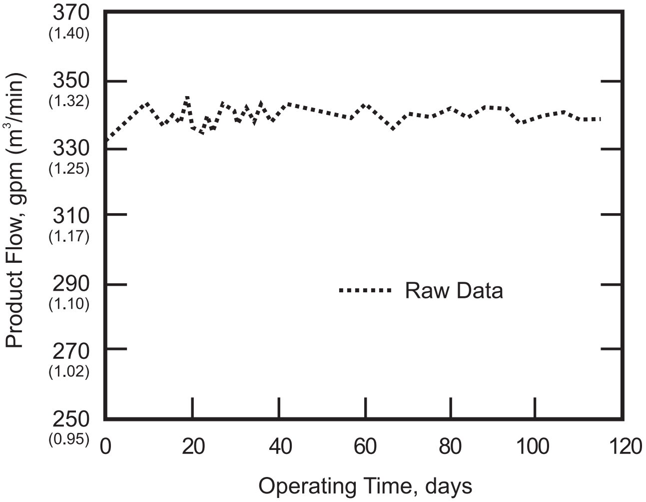

Figure 8.33 Observed permeate flow rate for actual RO system.

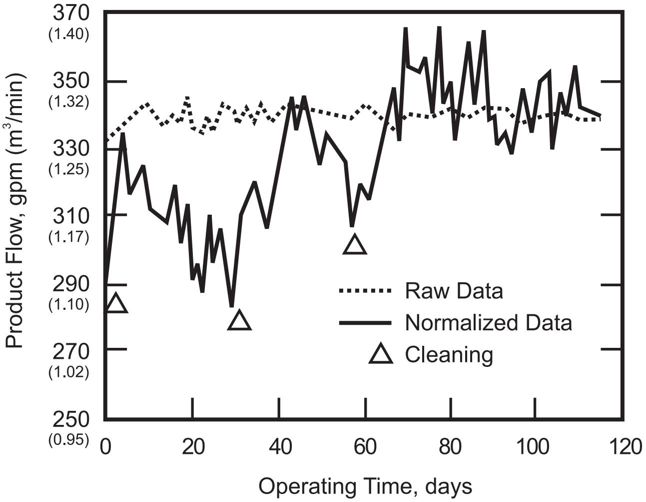

Figure 8.34 Observed and normalized permeate flow rate for same RO system as in Fig. 8.33.

Other Parameters of Interest Other parameters to monitor include pressure drop from the feed to the concentrate streams and normalized salt passage.

Nominal pressure drop should be about 21 to 28 kPa (3–4 psi) per membrane module, such that the first-stage pressure vessel with six membranes elements should have a pressure drop of about 124 to 165 kPa (18–24 psi) (note that the pressure drop per module is a function of the specific type of membrane employed and can vary from type to type). Pressure drops higher than this could be indicative of membrane fouling or scaling. Pressure drops approaching 345 kPa (50 psi) over a six-element single stage can lead to catastrophic failure of the membrane module via telescoping or cracking of the outer fiberglass shell.

Pressure drop can be normalized using Eq. (8.8):

$$\text{Normalized Differential Pressure} = \frac{\Delta P_{\text{actual}} \times (2\times \text{CF}_{su} + \text{PF}_{su})^{1.5}}{(2\times \text{CF}_{\text{actual}} + \text{PF}_{\text{actual}})^{1.5}} \tag{8.8}$$

where ΔP_{acutal} = actual differential pressure
CF = concentrate flow
PF = permeate flow
su = subscript for start up

Finally, salt passage can be normalized using Eq. 8.9:

$$\text{Percent Normalized Salt Passage} = \left[\frac{\text{EPF}_a}{\text{EPF}_s} \times \frac{\text{CFC}_s}{\text{CFC}_a} \times \frac{\text{STCF}_a}{\text{STCF}_s} \times \frac{C_{fa}}{C_{fs}}\right] \times \%\ \text{SP}_a \tag{8.9}$$

where EPF = average permeate flow divided by the number of membrane modules
STCF = salt transport temperature correction factor (from membrane manufacturer)
C_f = feed salt concentration
%SP = percent salt passage
CFC = concentration of the feed concentrate:

$$\text{CFC} = C_f \times \frac{\ln \frac{1}{1-Y}}{Y} \tag{8.9a}$$

where Y = product flow/feed flow
subscripts:
s = subscript for "standard" conditions
a = subscript for "actual" conditions

Common Causes of Reduced Efficiency: Fouling, Scaling, and Degradation

Primary concerns for NF and RO users are fourfold:

1. Quantity
2. Quality

3. Reliability
4. Safety

If water quantity requirements are not met, plant efficiency and operating costs are affected. In severe cases, plant shutdowns may be required. If water quality drops, downstream treatment equipment such as ion exchange polishers requires additional maintenance and expense. And, it is important to have a system that operates reliably and safely.

Keeping an NF or RO system running at optimum efficiency requires: scale and deposit control, fouling prevention, timely membrane cleaning, routine membrane replacement, and membrane integrity testing. All of these factors represent system costs (chemical, labor, energy, and maintenance). As membranes foul or scale, total operating cost for water production increases.

Membrane Fouling Membrane fouling is caused by particles and microbes that stick to feed channel spacers and to the surface of the membrane. Table 8.11 lists species that commonly foul NF and RO membranes. The table also lists generally accepted guidelines established to minimize the effect of these species.

Fouled membranes exhibit two key performance problems: high operating pressure (or low permeate flow) and high pressure drop.

Species	Measure	Generally Accepted Guidelines
Suspended solids	Turbidity	<1 NTU*
Colloids	Silt density index (SDI)	<5* (best practice, <3)
Organics	Total organic carbon (TOC), mg/L	<3
Color	Color units	<3 APHA†
Metals: Fe, Mn, Al	mg/L	<0.05
Hydrogen sulfide (H_2S)	mg/L	<0.1
Microbes	Dip slides	<1000 colony forming units/mL‡

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*Membrane manufacturer's warranty condition

†American Public Health Association

‡In RO concentrate

Table 8.11 Species That Commonly Foul NF and RO Membranes and Generally Accepted Guidelines to Minimize Fouling

Foulants form essentially a second layer through which feedwater must travel before reaching the membrane. Higher feed pressure is required to force water through this layer of foulants. Higher feed pressure naturally results in higher pressure drop. The foulant layer increases resistance to flow of water across the membrane, which is measured as additional pressure drop. Finally, foulants that 'stick' to the feed channel spacer greatly contribute to pressure drop through the system.

The phenomenon of fouling occurs primarily in the lead stage of an NF and RO system. This is because the lead membranes act as barrier filters to particulates that cannot pass through them. The lead membranes in the system are exposed to the particulates first in the process, so these membranes tend to foul more than the membranes that follow.

Colloids Fouling of membranes with colloidal silica and clays is a serious problem for NF and RO membranes, particularly those operating on surface water sources, where colloidal silica and clays are commonly found. Colloidal fouling is typically controlled by using pretreatment steps to remove particles to a silt density index (SDI) of less than five [see ASTM D4189-07 (reapproved 2014) for the SDI testing method]. Silt density index measures the fouling potential of the membranes with particulates larger than 0.45 μm.

It should be noted that when metals, such as iron, aluminum, or even calcium, coexist with silica, the respective silicates can form, even when the concentration of silica is below saturation. In the case where silicates can form, it is necessary to reduce the concentration of metals and/or silica via pretreatment so minimize this potential.

Organics Organic compounds, natural as well as synthetic, present in feedwater can cause NF/RO membrane fouling by various means. They can adsorb directly onto the membrane surface (adsorptive fouling), interact with other constituents of feedwater to produce gelatinous foulants on the membrane surface (organic deposit fouling), or promote growth of biofilm on the membrane (biofouling). The term organic fouling is used broadly here to include all types of fouling caused by organics, which is a frequent cause of NF and RO performance deterioration, and can account for 50% of membrane failures as shown in Fig. 8.35.

Potential sources of organics include natural organic matter (NOM such as humic and fulvic acids), synthetic chemical contaminants (especially in wastewater reclamation applications), and water treatment chemicals added to feedwater. Due to electrostatic interaction of cationic polymers with the anionic membrane surface, cationic polymer coagulants used in clarifiers or as filter aids can cause NF and RO membrane fouling when overdosed. Polymeric NF and RO antiscalants, if excessively overdosed, can deposit on membrane

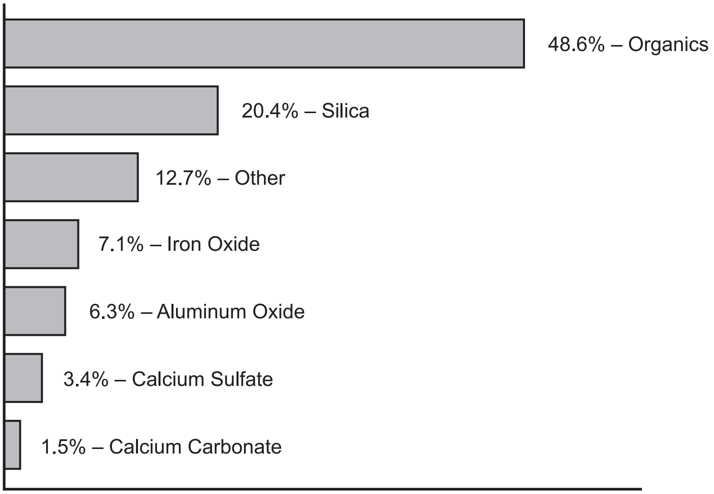

Figure 8.35 Typical causes of RO fouling, as gathered from 150 membrane autopsies, as presented at the 62nd Annual International Water Conference. (*Courtesy of IWC.*)

surfaces and cause fouling. Acid addition, while sometimes used for scale control, has been reported to increase propensity for NOM to cause membrane fouling.

Potential for water treatment organic chemicals to promote biofouling is often overlooked but has been studied. Organic chemicals provide organic carbon that can be metabolized by microbes as energy and carbon sources. Assimilable organic carbon (AOC) is generally accepted by the scientific community as the best indicator of biofouling potential of an organic compound.

Levels of AOC of various commercial antiscalants have been measured and found to vary as much as tenfold. To achieve highest RO system reliability in critical applications such as ultrapure water (UPW) production, it is desirable to minimize AOC contribution of water treatment chemicals.

True Color True color fouling due to lignins and tannins is irreversible; they adsorb onto the membrane polymer and foul the surface of the membrane. This leads to permanent flux decline and lost productivity of the system. True color is typically removed from NF and RO feedwater via clarification and sedimentation.

Metals Several metals and metallic compounds are of interest. Metal oxides, such as those of iron and manganese, can precipitate on membranes. Further, soluble forms of these metals can catalyze the oxidization of the membranes if an oxidant were present. Hydrogen sulfide is important in that it can release elemental sulfur, a very sticky element that is virtually impossible to remove from the membrane. These compounds are best reduced in feedwater using filtration through manganese dioxide media, such as pyrolusite, or sand coated by manganese dioxide (Greensand).

Biofouling Biofouling is the bane of existence for operators of NF and RO systems. Poorly operated pretreatment equipment, especially filters such as carbon filters, can promote biofouling by providing a large surface area as a breeding ground for microorganisms. The presence of organics can promote biogrowth on the membranes, as discussed earlier. The combination of organics within a carbon filter can create an incubator-type environment to foster proliferation of bacteria, and then can easily slough out of the filter into the NF or RO system.

Membrane biofouling is exceptionally difficult to control, because no oxidants can be used on the membranes to kill the organisms. Hence, the efforts to control biofouling are confined to pretreatment and on-time cleaning of the membranes. Pretreatment with oxidizers is typically used to control biogrowth in the feed system, with the hopes of minimizing the proliferation of microorganisms in the pretreatment system and on the membranes. Once biofouling has developed on the membrane, it is imperative that the membranes are cleaned on a regular schedule, as determined by the normalized performance of the system.

Membrane Scaling Scaling occurs as selective permeation of water through the membrane causes supersaturation and precipitation of sparingly soluble mineral salts, such as calcium carbonate and calcium sulfate. A method to avoid scale formation is to keep water recovery low. However, this means inefficient use of water and is not practical for industrial NF and RO plants, which must use water resources efficiently and avoid excessive concentrate waste.

Sodium regenerated ion exchange softeners technically offer a good method for scale control. However, using a softener can involve significant capital and operational expense. In addition, chlorides in brine regenerant discharge are becoming more regulated.

Other approaches to NF/RO scale control include acid and antiscalant dosing. Antiscalants are often the most attractive than acid due to the following advantages:

- Lower capital costs
- No handling of hazardous chemicals
- Applicable to a broad range of scales
- Better permeate quality

Antiscalants generally fall into one of two classes of compounds:

1. Threshold inhibitors (including crystal modifiers)
2. Dispersants

Threshold inhibitors prevent scaling by interfering with the crystal formation process. Dispersants, on the other hand, allow scale to form, but keep crystals small and interfere with ability of the crystal to deposit on a surface.

Polyphosphates such as sodium hexametaphosphate (SHMP) were used widely in the past, but their use has declined due in part to their tendency to hydrolyze and form orthophosphate that can lead to calcium phosphate scale problems. In addition, more effective antiscalant chemistries are available.

Polymeric dispersants are popular antiscalants; however, they are not compatible with many coagulant chemistries. Polymeric dispersants have limited calcium tolerance and can contribute to organic/biofouling due to their AOC content.

Phosphonates have proven to be significantly more effective scale control agents with higher tolerance to system variation. A wide variety of commodity and specialty phosphonates is available for scale control. Differences in performance, stability, and calcium tolerance are observed, depending on the phosphonate. System modelling helps determine which phosphonate is more appropriate for a given application.

Non-phosphonate chemistries that function through chelation are also used. This method of scale control is well documented, but effectiveness at substoichiometric levels can be limited.

Regardless of the type of antiscalant chosen for use in an NF or RO system, it is generally accepted that both underfeed and overfeed of antiscalant chemical can be detrimental to both the performance, and total cost of operating the system. Underfeed means not enough chemical is present to prevent fouling or scale formation. Overfeed can lead to membrane fouling, which can result in severe operating problems and increased operating costs. Often, antiscalant dosed to prevent fouling is the actual cause of it. Consequences of antiscalant underfeed and overfeed suggest that dosage control is critical to good and cost-effective operation of NF and RO systems.

Unfortunately, traditional methods for monitoring antiscalant feed such as timed draw down are inherently inaccurate, do not give a rapid response, and are not easily monitored. In fact, it is primarily due to limitations on antiscalant dosage control that costlier methods such as softening or pH control are used.

Chemical suppliers, plant operators, and NF/RO experts generally assume chemical dosage (such as antiscalant) to an NF or RO unit is constant. Field studies using fluorescent tracing of antiscalants demonstrates this assumption is often false. Fluorescence technology can reveal previously unseen variations in chemical antiscalant dosing.

While antiscalants perform well as the only means or controlling most scales, in some cases such as calcium phosphate and calcium fluoride scales, acid may need to be feed in addition to, or instead of the antiscalant, due to the relative inefficiency of antiscalants for these types of scale.

Membrane scaling is caused by precipitation of saturated salts onto the membrane surface and feed channel spacers. Table 8.12 shows species that commonly scale RO membranes. The table lists generally accepted guidelines established to minimize the effect of these species.

Scaled membranes exhibit three key performance problems:

1. High operating pressure (or low permeate flow)
2. High pressure drop
3. Low salt rejection

High pressure is required to force water through the additional scaling layer on the membranes in a manner similar to that described for fouled membranes (above). The effect of scaling on pressure drop is also similar to that of foulants, which may deposit on the feed channel spacer. The most interesting feature of scaled membranes is that apparent rejection by membranes decreases. This is because the concentration of the scaled species can be significantly higher at the membrane surface than in bulk solution. Since the membrane rejects based on what is contacting the membrane, intrinsic rejection is still the same, but rejection of the higher surface concentration means more of that species passes through the membrane than if the membrane were rejecting based on bulk concentration.

Species	**Measure**	**Generally Accepted Guidelines**
Silica (soluble)	mg/L	<200*
Barium, Strontium	mg/L	<0.05
Calcium carbonate	Langelier saturation index (LSI)	<0* < +2.5†

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*In RO concentrate without antiscalant feed

†In RO concentrate with antiscalant feed

Table 8.12 Species That Commonly Scale RO Membranes and Generally Accepted Guidelines to Minimize Scaling

Since scale is a concentration phenomenon, it follows that it would form at the back end of the NF or RO system where feed concentration is the highest.

Calcium-Based Scales Calcium carbonate ($CaCO_3$) is the most common scale to affect NF and RO membranes. Potential for forming calcium carbonate scale is measured using the Langelier saturation index (LSI). A positive LSI favors formation of this scale. LSI can be reduced using acid. Antiscalants are also effective in minimizing formation of calcium carbonate scale. Membrane manufacturers recommend that the LSI be limited to +2.5 or less when antiscalants are used to minimize formation of calcium carbonate scale; if antiscalants are not used, the LSI should be 0.0 or less.

Calcium phosphate ($Ca_3(PO_4)_2$) and calcium fluoride (CaF_2) scales can be more difficult to control than calcium carbonate, as their solubility constants are lower (10^{-33} and 10^{-11}, respectively, compared to 10^{-9} for calcium carbonate). Most antiscalants are not very effective for these scales, so acid is typically used either alone or with an antiscalant for control.

Sulfate-Based Scale Sulfate scales of calcium and trace metals such as barium and strontium will also scale NF and RO membranes. Such scales are also sparingly soluble, for example, solubility constants of barium sulfate and strontium sulfate are 1.1×10^{-10} and 3.2×10^{-7}, respectively. It should be noted that sulfuric acid, which is commonly used for reducing LSI or to address calcium phosphate or calcium fluoride scales, increases potential for forming sulfate-based scale. This is due to the additional sulfate to the solution this type of acid introduces. Care should be exercised when sulfuric acid is used for reducing the scaling potential of calcium-based scales.

Silica Formation of silica scale is dependent upon the temperature and pH of the water as well as the concentration of silica present. Silica decreases in solubility at lower temperatures and is least soluble between pH 6 and 9. Hence, operation at higher temperature and slightly acidic or highly alkaline conditions is preferred to minimize formation of silica scale. Another method of prevention is operating the system at a recovery that does not concentrate the silica to the point of saturation. In general, a concentration of about 160 to 180 mg/L is feasible at typical temperature and pH conditions for RO/NF systems. Silica scale is extremely difficult to remove from membrane surfaces, so prevention is the key method of control.

Note that at pH greater than 8, silica exists as the silicate anion (SiO_3^{-2}), which readily reacts with metals such as aluminum and iron to from insoluble silicates. These particles can foul an NF or RO membrane as discussed earlier.

Membrane Degradation Membrane damage or integrity loss, resulting in lower salt rejection and higher total dissolved solids (TDS) in NF or RO permeate, can be caused by:

- Chemical attack (e.g., oxidation by residual chlorine, frequent membrane cleaning
- Exposure to hydrocarbon solvents which dissolve the polyamide membrane layer)
- Physical stress (e.g., water hammer or excessive pressure drop due to excessive membrane fouling or scaling)

Methods to minimize membrane damage include complete feedwater dechlorination, proper mechanical design and operating conditions, and adequate pretreatment to reduce cleaning frequency.

Membrane degradation occurs when membranes are operated outside limits that have been established for safe RO operation. Table 8.13 lists conditions under which most RO/NF membranes will degrade.

Degraded membranes exhibit higher permeate flow and lower salt rejection than intact membranes. Operating pressure may also be lower.

Chlorine and other oxidizers attack (oxidize) most NF and RO membranes. With exposure to 1 mg/L free chlorine noticeable degradation can occur in as little as 200 hours. Most NF and RO membranes can tolerate from 200 to 1000 mg/L.h of exposure to chlorine; by this time, salt will have doubled. (Cellulose acetate membranes can tolerate up to 1 mg/L free chlorine continuously.)

Chloramines are generally less damaging to NF and RO membranes, typically up to 300 000 mg/L.h exposure to pure chloramine, by the time salt passage doubles. But since they are typically in equilibrium with free chlorine, degradation can occur much sooner. Additionally, free ammonia can also be present, which will swell the

Item	Measure	Value
Chlorine, free	mg/L	<0.02
Temperature	°C	45*
pH, normal operations	Units	3–10
pH, cleaning operations	Units	1–13*
Metals catalysts: Iron, manganese, cobalt	mg/L	<0.05
Hydrocarbon solvents	mg/L	0.0

*Check with membrane manufacturer; maximum pH and maximum temperature are related

TABLE 8.13 Conditions That Lead to RO Membrane Degradation membrane, leading to a *reversible* increase in salt passage. This phenomenon is a function of ammonia gas, and, therefore, occurs when the pH of the solution is greater than about 7.5. Most membrane manufacturers recommend keeping the pH at 7.2 or below minimize membrane swelling with ammonia gas.

Metals such as iron, manganese, and cobalt catalyze oxidation of NF and RO membranes if any oxidizers are present (chlorine, chloramine, ozone, hydrogen peroxide, etc.). This will significantly reduce the exposure time until salt passage doubles. Thus, the concentration of transition metals should be limited to avoid this catalytic degradation.

Most NF and RO membranes are safe to operate at pH between 2 and 10, depending on temperature. Outside of this range, membranes can begin to hydrolyze, which results in destruction of polymer chains that make up the membrane. The effect is enhanced at higher temperatures. The maximum pH a membrane can tolerate is lower at higher temperatures (Table 8.15). This is particularly important during membrane cleaning, where high temperature and high pH are beneficial for cleaning organics from the membranes.

Pretreatment

Pretreatment for NF and RO membranes, particularly for spiral wound modules, is much more involved than pretreatment for MF and UF membranes. Table 8.14 lists pretreatment guidelines and typical treatments for a number of potential foulants, scale formers, and degradation promotors.

Membrane Cleaning

Proper membrane cleaning is integral to keeping the membrane system operating well. Membranes should not be cleaned on a predetermined timetable but rather cleaned when needed. Cleaning on a timetable can result is either too frequent cleaning, resulting in premature degradation, or to infrequent cleaning, resulting in more permanent fouling and scaling. The proper time to clean is when normalized permeate flow drops 15% or pressure drop increases 15% from start-up conditions with new membranes. A good rule-of-thumb for cleaning membranes is that they are cleaned about four times per year or twelve times in the lifetime of the membrane. More frequent cleaning implies that the pretreatment system may be inadequate, and can lead to shorter membrane life.

Membranes are cleaned at pH extremes, ranging from 2 to 13. Many times, additives such as surfactants or chelants, like ethylenediaminetetraacetic acid (EDTA), are included to aid in cleaning membranes. In general, high pH cleaning serves to remove organics, microbes, and sulfate-based scales. Low pH cleaning removes iron oxide and calcium carbonate scales. It is typically recommended that the high pH cleaning be conducted first, as low pH cleaning has

Item	F,S,D[a]	Units	Guideline	Pretreatment Techniques
Suspended solids	F	NTU	<1[b]	Multimedia filtration
Colloids	F	SDI	<5[b]	Multimedia filtration + coagulant Membrane filtration (MF, UF)
Hydrogen sulfide	F	mg/L	<0.1	Oxidation + pyrolusite filtration
Organics (TOC)	F	mg/L	<3	Clarification Carbon filtration
True color	F	APHA or Pt-Co	<3	Clarification
Transition metals (iron, manganese)	F, D	mg/L	<0.05	Oxidation + pyrolusite filtration
Aluminum	F	mg/L	<0.05	UF + acidification to pH 6.5
Microbes	F	CFU	<1000[c]	Membrane filtration (MF, UF) Oxidizers
Calcium carbonate	S	LSI	<0.0[d] < +2.5[e]	Acid
Metals (barium, strontium)	S	mg/L	<0.05	Sodium softening Antiscalants
Silica (soluble)	S	mg/L	140–200[f]	Antiscalants Acid (< pH 5) or caustic (> pH 9) Heat Reduced system recovery High efficiency RO (HERO) process
pH	D	-	CA: 4–6 PA: 2–12	Acid or caustic
Temperature	D	°C	CA: < 35 PA: < 45[g]	Heat exchanger
Oxidizers	D	mg/L	0	Carbon filtration Sodium bisulfite

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[a] F = fouling, S = Scaling, D = Degradation
[b] Meets membrane manufacturer's warranty
[c] In the RO/NF concentrate stream
[d] Without antiscalant
[e] With antiscalant
[f] In RO/NF concentrate stream, function of pH and temperature
[g] Standard spiral wound membrane modules

Table 8.14 Pretreatment Guidelines for Spiral Wound RO/NF Membranes

Temperature	pH*
77°F (25°C)	Up to 13
95°F (35°C)	Up to 12
113°F (45°C)	Up to 11

*Check with membrane manufacturer

Table 8.15 Temperature and pH Allowed During Membrane Cleaning

been shown to "set" or harden organic and biological materials, which makes it more difficult to remove them from NF and RO membranes.[19]

Membranes should be cleaned at elevated temperatures. Table 8.15 lists the temperatures and pH combinations that are used to clean membranes. Cleaning outside these ranges can accelerate hydrolysis of the membranes.

An NF or RO skid should be cleaned one stage at a time using a separate cleaning skid and pump. This will make sure that all the membranes are cleaned at the appropriate flow rate and pressure for optimal results. A typical protocol for a 203 mm (8 inches) diameter pressure vessel is to recirculate fresh cleaning solution through each stage individually at about 7.9 to 9.1 m^3/h (35–40 gpm). The first couple of minutes of recirculation should be discarded. If the entire cleaning solution volume turns dark immediately as it is recirculated, it should be discarded and a new batch should be prepared. After recirculation of 45 to 60 minutes, the solution is then left to soak for up to 12 hours for stubborn fouling or scaling. Final recirculation for a 203 mm (8 inches) diameter pressure vessel should be 10 m^3/h (45 gpm). It is important that the cleaning pump be sized to handle 10 m^3/h (45 gpm), while producing no more than about 414 kPag (60 psig) as no permeate should be made during cleaning. Any permeate that is generated should be sent back to the cleaning tank. The membranes should then be rinsed with permeate or higher quality water at ambient temperature, in preparation for the next cleaning solution or for return to service. Note that a high pH cleaning solution tends to "loosen" the membranes, resulting in temporary high flux and high salt passage. A low pH cleaning solution "tightens" the membrane, resulting in a temporary low flux and higher rejection. The cleaning solution should be discarded after each stage.

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[19] Broden, C., Gilbert, C., "Pushing the Limits: Improved RO Cleaning Recommendations," Presented at the International Water Conference, 2007.

Method	Advantages	Limitations
CIP	On-site Fast	Less efficient cleaning Capital cost of skid Chemical handling
Outsourced, off-site	Expert service Documentation of results	Costlier per cleaning Requires backup membranes

Table 8.16 Advantages and Limitations of CIP Versus Outsourced Off-Site Membrane Cleaning

Membranes can be cleaned in place (CIP) or sent out for cleaning. Table 8.16 lists the advantages and limitations for each option. In general, the larger the NF or RO system, the more likely the membranes are cleaned on-site.

Troubleshooting

Virtually all NF and RO systems eventually experience problems. Low permeate quality and quantity and high operating pressures seem to be the most common ailments afflicting these systems. There are several techniques available to troubleshoot NF and RO systems:

- Mechanical inspection
- Water analyses and mass balance
- Data monitoring and normalization
- Comparison of actual performance with performance projections
- Profiling and probing
- Membrane integrity testing
- Membrane autopsy

Mechanical Inspection Mechanical inspection involves checking all instruments and probes as well as valves and fittings to make sure they are all calibrated and working properly. Checking pretreatment equipment is also important, to make sure these are operating as designed, and that the design is appropriate for the application. Channeling of water through pressure vessels can occur when the feed flow rate is too high or too low, or the media inside the vessel is dirty. Channeling results in poor removal of contaminants from the feed, which then travel on into the membrane system.

Checking to make sure the vessel was designed properly for the application is also important. For example, a carbon filter designed for chloramine removal should be sized significantly larger than one designed for chlorine removal.

Water Analyses and Mass Balance Water samples should be collected and analyzed for membrane feed, concentrate, and permeate streams. Mass balances can then be calculated for species of interest. If the amount of a species in the sum of the concentrate plus permeate, is less than that in the feed, there could be some deposition of this species within the membrane module. That this is a mass balance so the amount of a species in the feed, permeate, or concentrate is determined by multiplying the concentration by the solution flow rate.

Also, checking the water analysis periodically to make sure no new contaminants have appeared, or that the concentrations of contaminants have not changed is critical. Recall that rejection is a percentage, so that if the concentration of a species increases in the feed, its concentration will also increase in the permeate.

Data Monitoring and Normalization Data should be collected and normalized as described earlier. Using normalized data is the only true way of comparing performance over time and determining condition of the membranes. Pressure drop should be monitored as another means of determining whether membranes are fouled or scaled. Pressure drop should average about 4 to 6 psi (~27–41 kPa) per element, so that a six-element pressure vessel should have a pressure drop of about 24 to 30 psi (~165–207 kPa). Maximum pressure drop per six-element vessel is 50 psi (~345 kPa); higher pressure drop can lead to physical damage of the module and membranes within. High pressure drop over the first stage is usually indicative of membrane fouling, while high pressure drop over the last stage is usually indicative of scaling.

Comparison of Actual Performance with Projected Performance Comparison of projected performance and actual performance can be very useful. The projections give an indication of what the operating pressure should be, as well as pressure drop, and permeate quality. Most membrane manufacturers indicate that the actual operating pressure and permeate flows should be within ±15% of the projections; permeate concentration should agree with the projection. It should be noted that projection and actual performance should be compared at the same temperature, as temperature affects performance. For example, higher temperature means lower pressure is required to pump the same amount of water through the membrane. Higher pressure also results in lower permeate concentrations, (better quality).

Profiling and Probing Profiling and probing techniques are used to identify leaks in the RO system due to breaches in the membrane from degradation, or damaged O-rings on inter-connectors or end caps. These techniques can also be used to detect membrane scaling.

If an RO skid is exhibiting low permeate quality, it should be subjected to profiling. Profiling involves measuring conductivity out of each individual pressure vessel permeate sample port. The pressure vessels exhibiting high conductivity should then be probed. Probing requires that a 6.4 mm (0.25 inch) diameter tubing be snaked down through the permeate channels in all the membranes loaded in the pressure vessel of interest. While the RO is running, a sample of water running through the tubing from the other end of the pressure vessel is measured for conductivity. The tubing is then extracted about 0.5 m (20 inches) and conductivity is measured again. This is repeated until the tubing reaches the end of the pressure vessel. These data are then graphed, an example of which is shown in Fig. 8.36.

A well-operated system will show a gradual increase in concentration over the length of the pressure vessel. Spikes in the graph correspond to locations where there is higher salt passage. This can be due to O-rings failure if the spike occurs at the multiples of 1 m (40 inches), which corresponds to the space between membrane modules. Or, it can be due to damaged membranes, if the spike occurs within the length of a module. A smooth curve that is steeper than that for nominal operations is indicative of membrane scaling.

Membrane Integrity Testing Two in-situ tests can be conducted to determine if membranes have been damaged or degraded:

Vacuum Decay Test This test identifies leaky membrane modules. The test requires isolation of an entire pressure vessel. A vacuum is applied to the pressure vessel and to modules within, and the rate of decay in pressure is measured. A decay rate faster than about 10 kPa/min (1.5 psi/min) is indicative of damage. Refer to American Society of Testing and Materials (ASTM) Standards D3923 and D6908 for a complete review of this technique.

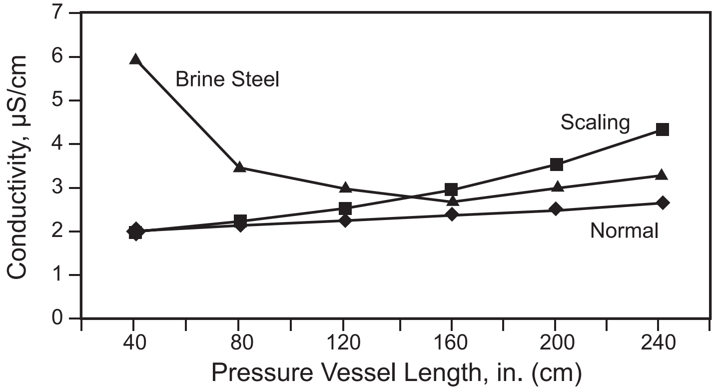

FIGURE 8.36 Data results from RO vessel profiling.

Rhodamine B Test This test also identifies damaged membranes. Rhodamine B dye is fed to pressurized RO feedwater and should be rejected 100% if the membrane is intact. If permeate turns pink, dye is leaking through damaged membranes.

Membrane Autopsy Membrane autopsy is a destructive test, and therefore, it should be considered a last resort in determining the cause of membrane failure. Several tests are involved to determine the nature of degradation, fouling, or scaling:

Fujiwara Test This test measures the degree of halogenated organics in a membrane sample. A positive test is indicative of halogen attack on the membrane polymer.

Methylene Blue Die Test This test is used to determine if there is any damage or leaks to the membrane, whether from chlorine (oxidative) or other causes. The die is rejected 100% by an intact RO membrane, so any membrane showing blue die on the permeate side has been damaged. However, some NF membranes do pass the methylene blue die, so interpreting the results for this test for NF membranes can be difficult.

Microbial Analysis Deposits on the membrane are analyzed for microorganisms. The organisms may be further analyzed into their specific types.

Spectroscopy Several different methods are available for membrane autopsy evaluation utilizing spectroscopy.

- Standard light microscopy is used to determine morphology of materials on the surface of the membrane.
- Scanning electron microscopy (SEM) is used to determine morphology of deposits on the membrane.
- Energy dispersive X-ray fluorescence (EDXRF) is used to determine compounds or elements present in membrane deposits.
- Inductively coupled plasma atomic emission spectroscopy (ICP-AES) is used to determine the amount of metals and silica in a membrane deposit.
- Electron spectroscopy for chemical analysis (ESCA) is used to identify organically bound materials on the membrane surface.

Electrochemically-Driven Membrane Separation Process: Electrodeionization/Continuous Electrodeionization

Electrodeionization (EDI), is a family of processes which includes electrochemical ion exchange, capacitive deionization, and continuous electrodeionization (CEDI), also known as continuous deionization (CDI).

While EDI processes have been researched since the 1950s, CEDI is a relatively recent addition to the field of membrane separations, having been first commercialized in the late 1980s. CEDI is an electrochemically-driven membrane separation technique used for removing trace ionizable dissolved solids from water. Separation is affected with ion exchange membranes and resins via an electrical current.

CEDI systems were developed to replace conventional ion exchange, specifically mixed bed polishers following RO. Mixed-bed water quality can be achieved with CEDI without the need for regeneration chemicals and waste neutralization.

Since the early 1990s, the power industry has been a leader in employing RO/CEDI technology for boiler makeup water. Other industries currently employing CEDI technology include pharmaceuticals and semiconductors, laboratories, food and beverage, and chemical. There have been also some inroads into wastewater treatment and recycling applications. The use of CEDI eliminates the need for storing and frequent handling of relatively large volumes of acid, caustic, and regeneration waste that would be required if traditional ion exchange were used.

Theory of Operation

Figure 8.37 shows an expanded view of a CEDI stack, which consists of layers of cation- and anion-exchange membranes separated by spacers that act as alternating product and reject compartments. Traditionally, every other compartment is filled with ion exchange

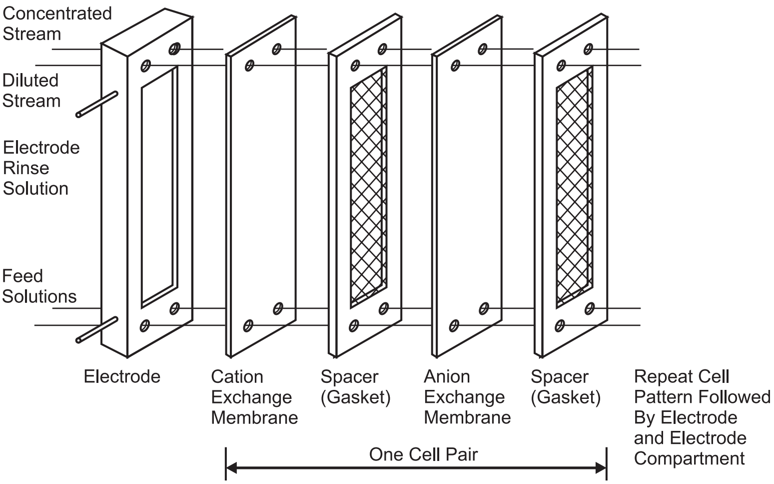

FIGURE 8.37 Expanded view of CEDI stack.

resin (the diluting compartment). However, with the newer "all-fill" configurations, all compartments are filled with resin. The resin is used primarily to enhance the transport of ions through the compartments, and as a substrate for splitting water into hydrogen (H^+) and hydroxyl ions (OH^-) used for the continuous regeneration of the resins. At one end of the stack is the cathode, and the other end of the stack has the anode. An electrical potential is applied to the stack, typically 100–600 volts DC at 3 to 20 amp. This electrical field drives cations toward the cathode and anions toward the anode.

Cations readily pass through cation-exchange membranes but not through anion-exchange membranes. Likewise, anions pass through anion-exchange membranes but not through cation-exchange membranes. In this manner, every other compartment becomes dilute in ions, while the other compartments become concentrated in ions (Fig. 8.38). The resin serves to facilitate the transfer in low ionic strength solutions. Additionally, at the low salinity or outlet portion of the resin bed, the current dissociates water in the diluting compartment into hydrogen and hydroxyl ions, which serve to regenerate resin at the outlet of the resin bed. This allows for production of multi-mega-ohm water from a CEDI system.

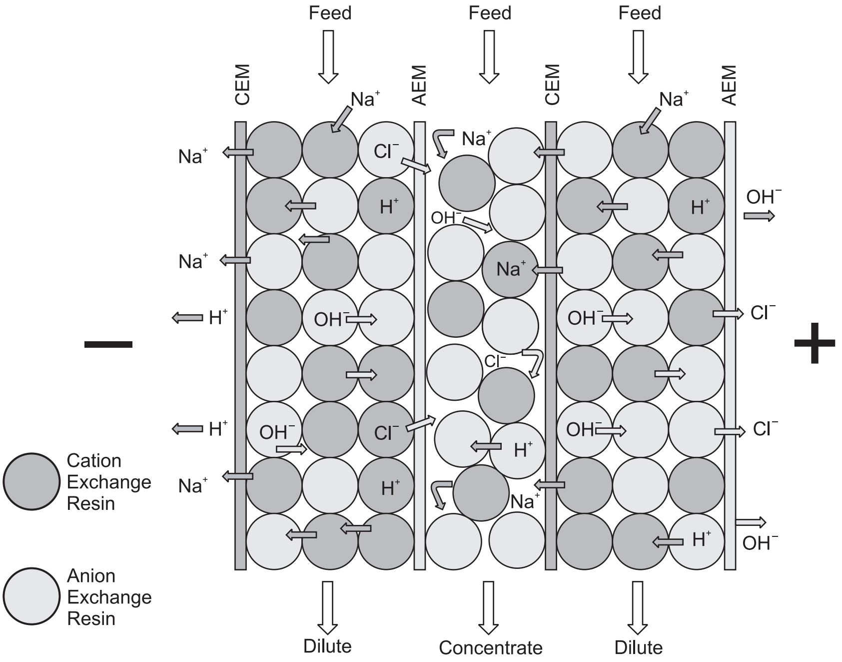

Figure 8.38 Cross section of an "all-filled" CEDI cell. (*Courtesy of Jonathan Wood*.)

Specifically, CEDI can produce 18 MΩ water at up to 99% water recovery, with 95% rejection of boron and silica and 99% rejection of sodium and chloride.

Advantages of the newer, all-fill configuration are several. First, recycle of concentrated solution is not required. Recycle increases the mass transfer rate and minimizes the potential for fouling and scaling of the membranes. However, utilizing water dissociation to regenerate resin with the all-fill configuration, mass transfer rates are significantly improved, and weakly ionized species such as carbon dioxide and silica are more readily removed from solution. Additionally, all-fill configurations are much less complex in design, as the recirculation mode requires additional hardware, including motor starters, controls to balance pressure in all streams, and controls to prevent pump cavitation.

Membrane modules

Continuous electrodeionization modules are available in plate-and-frame [stacked-disk (see Fig. 8.37), and rectangular-plate configurations], as well as in the spiral wound configuration (Fig. 8.39). Plate-and-frame devices resemble plate-and-frame heat exchangers, with alternating compartments of cation/anion-exchange membranes, and product and reject compartments located between end plates and electrodes. Spiral wound devices resemble the RO spiral wound configuration, but with the center permeate tube replaced with an

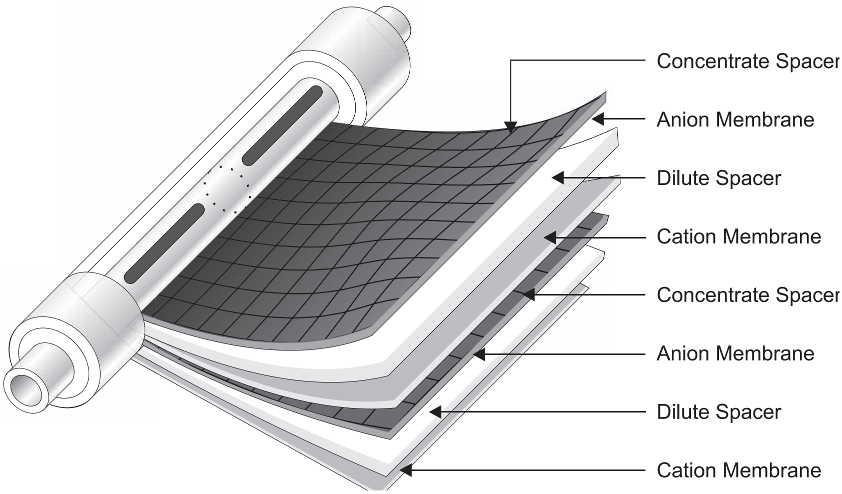

Figure 8.39 Spiral wound CEDI module. (*Courtesy of Dow Water and Process Solutions*.)

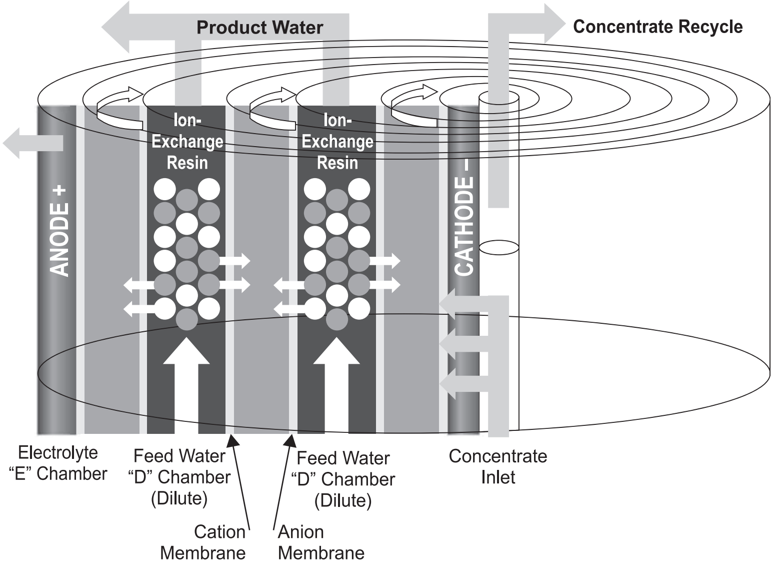

Figure 8.40 Spiral wound CEDI cross section. (*Courtesy of Dow Water and Process Solutions*.)

electrode (Fig. 8.40). Commercial modules are available in sizes from 0.2 m^3/h (1 gpm) up to about 18 m^3/h (80 gpm). Typical module life is up to five years.

Cell Spacing

Spacing of the diluting (product) compartment between ion-exchange membranes can be either thin-cell or thick-cell[20], with thick-cell devices exhibiting a spacing of 8 to 10 mm, and thin-cell spacing of about 1.5 to 3.5 mm. The thin-cell devices typically contain mixed-bed resin in the product compartments, while thick-cell devices are more suited to lower TDS waters where cation and anion resins are located in separate regions of the compartment.

Resins

Typical ion exchange processes rely on the capacity of the resin. The CEDI resins are optimized for their ability to rapidly transport ions to the ion exchange membrane, not selectivity. The combination of the membrane and resin must be chosen so that the electrochemical splitting of water can occur within the device, so that regeneration can happen.

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[20] Gifford, J., Atnoor, D., "*An Innovative Approach to Continuous Electrodeionization Modules and System Design for Power Applications*," Presented at the International Water Conference, 2000.

Parameter	General Requirement
Feedwater type	RO permeate quality
Conductivity	<40 μS/cm
Carbon dioxide	<5 mg/L
Silica	<0.5 mg/L
Fe, Mn, H_2S	<0.01 mg/L
Total chlorine	<0.05 mg/L
Free chlorine	<0.05 mg/L
Total hardness	<1.0 mg/L $CaCO_3$ (<0.5 for some applications)
Total organic carbon (TOC)	<0.5 mg/L
pH	4–11
Temperature	5–45°C (41–113°F)
Pressure	172–689 kPag (25–100 psig)

TABLE 8.17 General Feedwater Quality Requirements for CEDI Systems

Pretreatment

CEDI requires a significant amount of pretreatment to prevent damage to the module, and fouling and scaling of membranes. Table 8.17 lists general feedwater quality requirements for CEDI systems. As always, one should follow the requirements for the specific device being used. To achieve these requirements, virtually all CEDI systems are preceded by RO. In some cases, double-pass RO, sodium softening followed by RO, or RO followed by sodium softening is necessary to meet the feedwater quality requirements.

Select Conditions That Can Influence CEDI Performance

Carbon Dioxide Just as with ion exchange systems, carbon dioxide (CO_2) in CEDI feedwater imparts an ionic load on the system. In some cases, a concentration of 10 mg/L may be enough to prevent the system from meeting boiler feedwater requirements. Typically, carbon dioxide removal systems, including gas separation membranes, are employed to remove CO_2 from CEDI feedwater.

Temperature CEDI systems operate best within a temperature range of 5 to 45°C (41–113°F). At lower temperatures, kinetics and diffusion rates are slower, and electrical resistance increases. This results in an increase in voltage along with a decline in performance. Materials of construction limit the upper end of the temperature range. Many materials used to construct CEDI cells cannot tolerate high temperatures and degrade, resulting in leaks, poor performance, and higher energy requirements.

Total Organic Carbon Organics foul ion exchange resin, particularly anion resin. This results in poor performance and an increase in electrical requirements.

Cleaning

Chemical cleaning of CEDI membranes is generally undertaken when the electrical resistance of the unit increases or the product quality decreases. Some of the substances that cleaning helps to remove include, scale, organics and biological material. Common cleaners include sodium chloride, sodium hydroxide, and hydrochloric acid. The CEDI modules can tolerate pH ranging from 1 to 14, so aggressive cleaning is possible, as is overnight soaking at pH extremes to remove stubborn foulants. As with RO membranes, the high pH cleaning should be conducted prior to the acidic cleaning to minimize the setting of organics and biological material on the membrane.

Monitoring and Troubleshooting

Unlike RO/NF, there is no data normalization of CEDI data. Rather, online instrumentation is used to check performance of the system. Conditions that should be regularly monitored for troubleshooting include:

Feed Pressure—Should not exceed maximum rating for the device, typically around 4.0 to 6.9 bar (60–100 psig).

Product Pressure—The pressure of the product stream should be maintained at about 0.14 to 0.34 bar (2–5 psi) higher than the reject stream to minimize the negative effects on the product quality should a cross-leak occur.

Recovery—The recovery of the CEDI system should be monitored to make sure that no hardness deposits are occurring in the system. Typical recovery for CEDI ranges for 80 to 95% and is generally limited by feedwater hardness.

Temperature—Feedwater temperature will affect the performance of the system, as discussed previously.

Voltage—An increase in voltage required by the system can be indicative of fouling of the membranes. As discussed previously, temperature can affect voltage, so any changes in voltage should be compared against temperature to determine if fouling or a temperature decrease is responsible for the voltage increase. If temperature has not decreased, the increase in voltage indicates that fouling or scaling has occurred, and a chemical cleaning is required to restore performance.

Feedwater Analysis—Analyses of the feedwater quality to the CEDI unit should be conducted frequently. Species to test for include free and total chlorine, TOC, and total hardness. The values for these species should all meet the requirements for feedwater as set forth by the device manufacturer.

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SECTION 3.2

Applications—Steam Generation

Chapter 9
Boiler Systems

Chapter 10
Oxygen Removal

Chapter 11
Boiler Feedwater Treatment

Chapter 12
Turbines

Chapter 13
Condensate Systems

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CHAPTER 9

Boiler Systems

Water, when sufficiently heated, is converted to its vapor form, steam. Because of its heat or energy content and because it is an easily transportable fluid, steam is an efficient means of moving energy from one point (the source or boiler) to its intended end use (heating, electric power generation, etc.). Here, the energy contained in the steam is transferred to an operation requiring heat such as a chemical reaction or heating of a fluid, or is converted into work such as in driving a piston or turbine. Steam finds use in a wide variety of applications: comfort heating in buildings; process heating in many industries such as food, petroleum, chemical processing, and pulp and paper; and electric power generation.

Many things can happen to the water and steam en route to the final destination. Steam may be lost; some is condensed and returned to its liquid state. Some of the highly concentrated boiler water must be removed to limit scale deposition and corrosion. Water may be added to compensate for these losses or to replace water removed deliberately.

Steam Generation

Steam is produced in a steam generator or boiler, which is usually heated by the burning of coal, oil, gas, wood waste, or organic byproducts of a plant process. Steam is also produced at some electric utility plants by nuclear reaction. Water is boiled, and the vapor is discharged at a controlled temperature and pressure. As vapor leaves the boiling water, the dissolved solids originally in the water are left behind. A simple conceptual diagram of the steam generation section of a boiler system is shown in Fig. 9.1.

The boiler water left behind becomes increasingly concentrated, and eventually reaches a level where further concentration could cause scale or deposits to form or result in problems with steam quality or steam purity. This highly concentrated water must be removed to prevent scale deposition or corrosion. This removal process is known as blowdown. Additional water (makeup) must be added to the

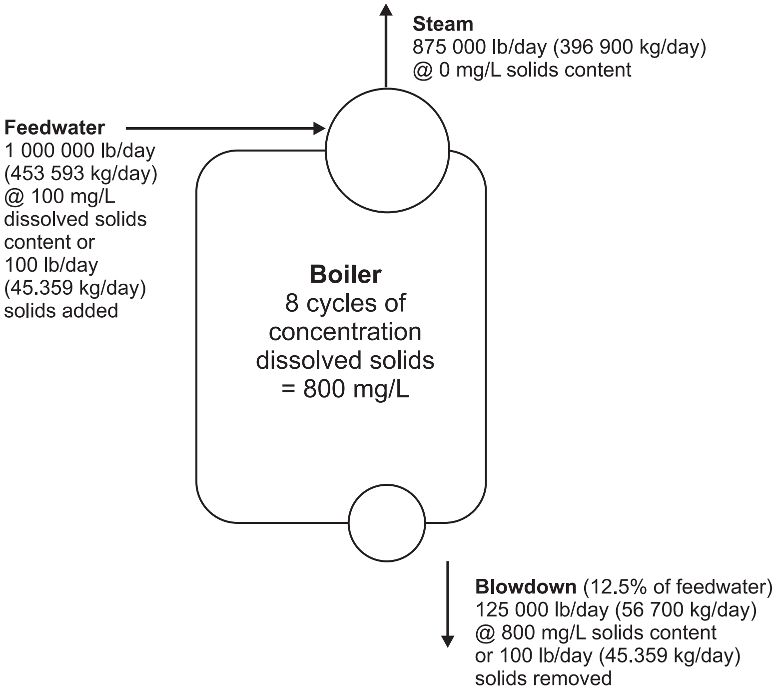


Figure 9.1 Simple boiler material balance.

system to replace any steam or condensate not returned to the boiler, as well as the blowdown withdrawn from the boiler.

In the steam generator, water circulates in a pattern produced by the path of heat from the fuel through a network of boiler tubes, as illustrated in Figs. 9.2, 9.3, and 9.4.

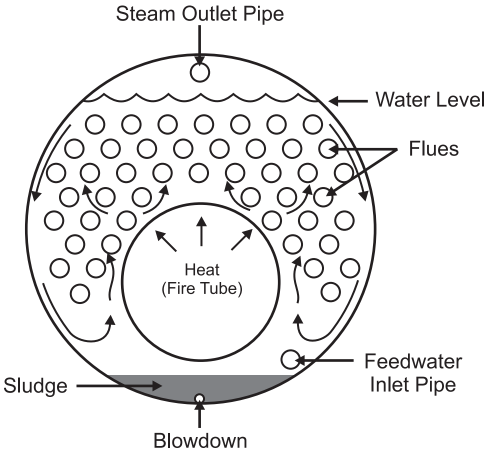


Figure 9.2 Water circulation in a firetube boiler.

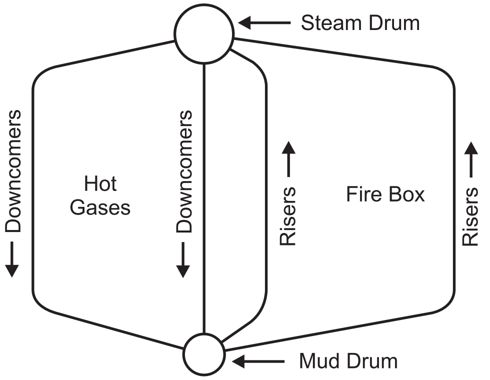


Figure 9.3 Circulation in a two-drum watertube boiler.

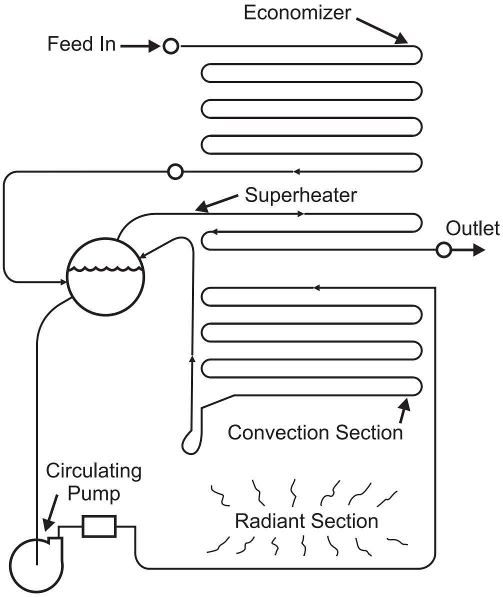


Figure 9.4 Pumps assist in circulating water through a boiler when natural circulation is restricted by limited density difference because of pressure or elevation.

Condensate

When the steam delivers its heat to the point of use, depending upon pressure, it gives up between 210 to 1100 Btu/lb (488–2560 kJ/kg) as it condenses at the prevailing temperature, and returns to the lower energy level state of a liquid. Condensate is usually free of mineral contamination and contains heat, so it is a very valuable source of water. As much condensate as possible is collected and returned to the boiler because of its heat value.

As condensate forms, it must be drained to a reservoir (receiver) for return to the feedwater stream, usually at the deaerator. The drainage system, which is usually separate for each major steam user and condensate producer, consists of the following components:

- Steam traps to maintain backpressure and to permit condensate flow but not steam flow
- Collection tanks, which are usually vented to a low-pressure steam line or to the atmosphere
- Pumps to deliver the condensate to the deaerator or another point in the system

Steam or Condensate Losses

Very little steam or condensate is lost in a large electric utility station, except in a few operations that are usually intermittent such as soot blowing. In an industrial plant, however, it is quite common to lose 30 to 80% of steam, condensate, or both. Major causes of steam and condensate loss include consumption in the process, contamination of condensate through product inleakage, and pipe leaks. Other losses might result from erratic demands for steam by different operating departments, which can upset the heat balance and cause a loss of low-pressure steam because of a momentary or seasonal inability to use it.

Economics also play a role; the cost of installing condensate collection systems with piping, especially for minor use, is often not justified by the value of recovered condensate, particularly in plants where piping installation is difficult or fuel costs are low.

Makeup

Fresh water of acceptable quality must be added to compensate for losses. Hence, this fresh water is called makeup. Scale-forming minerals are generally removed from makeup by precipitation softening, ion exchange, or reverse osmosis before it is added to the boiler system. Waste heat streams, such as blowdown, may also heat makeup before it is added to the boiler system. Figure 9.5 shows a simple but typical boiler makeup water system.

Concentration by Evaporation

Even after primary treatment, makeup still contains dissolved solids, such as traces of hardness, and variable amounts of sodium, alkalinity, and silica. Makeup must be treated to reduce this dissolved matter to acceptable levels (depending on the pressure of the boiler and the uses of the steam); the choice of pretreatment technology is based principally on economics.

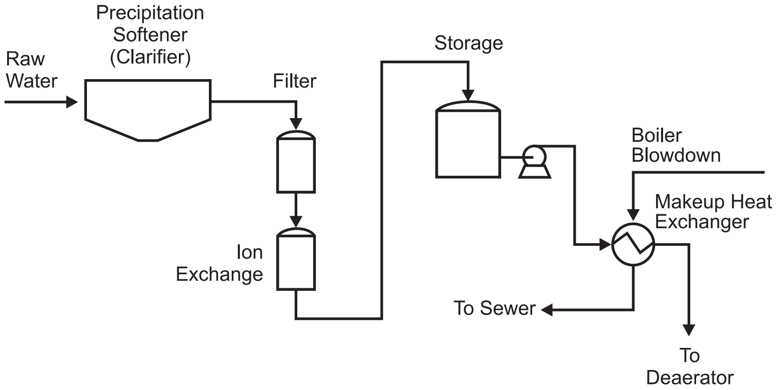


Figure 9.5 Typical boiler makeup water system.

As relatively pure steam is withdrawn from the boiler, the solids left behind concentrate in the boiler water. Based upon pressure and steam purity, there is a limit to the maximum concentration levels the boiler can tolerate. Exact limits are impossible to determine; however, several consensus guidelines have been gathered based upon operating experience, laboratory data, etc., and have been published by various organizations including the American Society of Mechanical Engineers (ASME), the American Boiler Manufacturing Association (ABMA), and Nalco. In addition to the above, there are other references such as the Electric Power Research Institute (EPRI), the VGB (a German organization of large power station operators), the Association of German Technical Inspectorates (VdTÜV), the British Standards Institute (BSI), and the Japanese Industrial Standard (JIS). Each of these may approach the problem of defining feedwater and boiler water concentrations from a different perspective; therefore, the recommended values may differ, depending on the source. Remember that the values provided are suggested guidelines and that actual boiler specification limits must be established on an individual basis, depending on the desired steam purity and end use requirements.

Blowdown

Blowdown is a deliberate loss of boiler water intended to keep the critical components dissolved in the boiler water from over-concentrating. Blowdown must also be replaced by makeup, so that the following relationship applies:

$$\mathrm{TM} = \mathrm{SL} + \mathrm{CL} + \mathrm{BL} \tag{9.1}$$

where TM = total makeup
SL = steam losses
CL = condensate losses
BL = boiler water losses

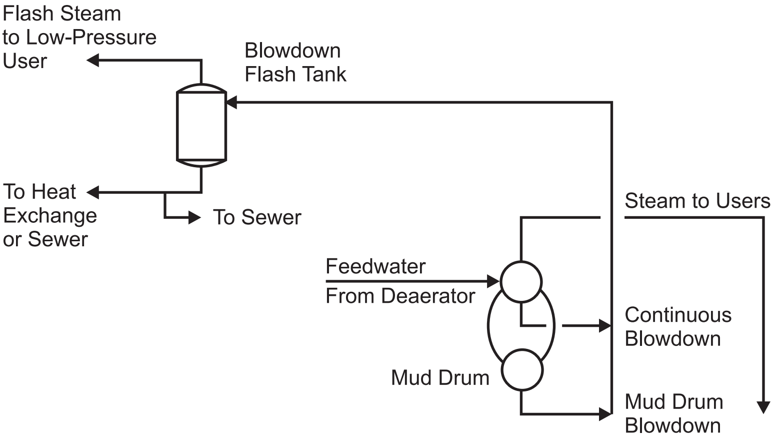


Figure 9.6 Typical boiler blowdown system.

In low-pressure units or in boiler systems that do not produce large quantities of steam, blowdown is often sewered. In larger systems, considerable amounts of blowdown contain valuable heat, which can be recovered in flash tanks and heat exchangers. Flash tanks extract low-pressure steam and send it to various users, which may include the deaerator or lower-pressure processes. Water from the flash tank still has considerable heat value and may be used further to preheat incoming makeup water. Figure 9.6 shows a blowdown system and possible schemes. Calculations showing the relationship between blowdown and feedwater are presented later in this chapter.

Feedwater

Makeup and return condensate combine with deaerator steam to become boiler feedwater. A simple diagram showing a typical feedwater system is presented in Fig. 9.7. ASME has established

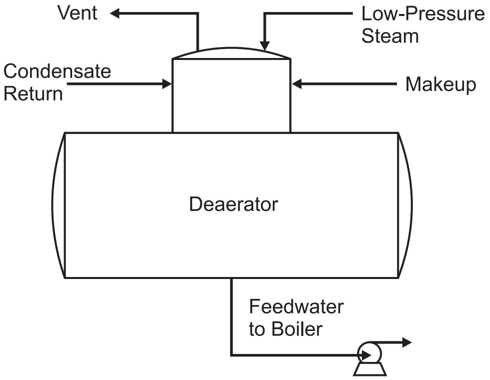


Figure 9.7 Typical boiler feedwater system.

guidelines for feedwater quality, and the reader is referred to these guidelines for details.

Mathematical Relationships

All of the flows, input and output, in a typical industrial boiler system are shown schematically in Fig. 9.8. In the system illustrated, steam discharges from a boiler to a turbine and other users. All or part of the steam may be condensed in the condenser; some may be extracted for process use. Other steam may go directly to a process, where it may be lost or may become contaminated and must be discarded. Still other steam may go directly to a process and then be condensed and returned to the boiler. The relationships among blowdown, makeup, and feedwater are discussed in detail here and are illustrated in the materials balance diagram in Fig. 9.1.

Blowdown and Makeup

Blowdown and makeup are usually expressed as a percentage of feedwater. (They can also be calculated as a percentage of steam flow; however, this book will use the feedwater calculation convention.) When the flow rates of these streams are known, the following equations can be used to describe their relationship:

$$\%\text{BD} = (100)(\text{BD})/\text{FW} \tag{9.2}$$

$$\%\text{MU} = (100)(\text{MU})/\text{FW} \tag{9.3}$$

where BD = blowdown mass flow, lb/h (kg/h)
MU = makeup mass flow, lb/h (kg/h)
FW = feedwater mass flow, lb/h (kg/h)

Many times, actual quantities of blowdown, feedwater, and makeup are not known. In such cases, percentages of blowdown and makeup can be calculated based upon the concentration of a particular dissolved solid or total dissolved solids (TDS) in the various streams.

$$\%\text{BD} = (100)(\text{TDS}_{\text{FW}})/\text{TDS}_{\text{BD}} \tag{9.4}$$

where TDS_{FW} = TDS in feedwater, mg/L
TDS_{BD} = TDS in blowdown, mg/L

It is very important that when dissolved solids are used to measure the percent blowdown, the feedwater sample must be taken after all chemicals have been added to the system. If conductivity is used for the measurement of dissolved solids, the boiler water sample must first be neutralized before measuring the conductivity, because any hydrate (O) alkalinity will greatly increase the conductivity of the

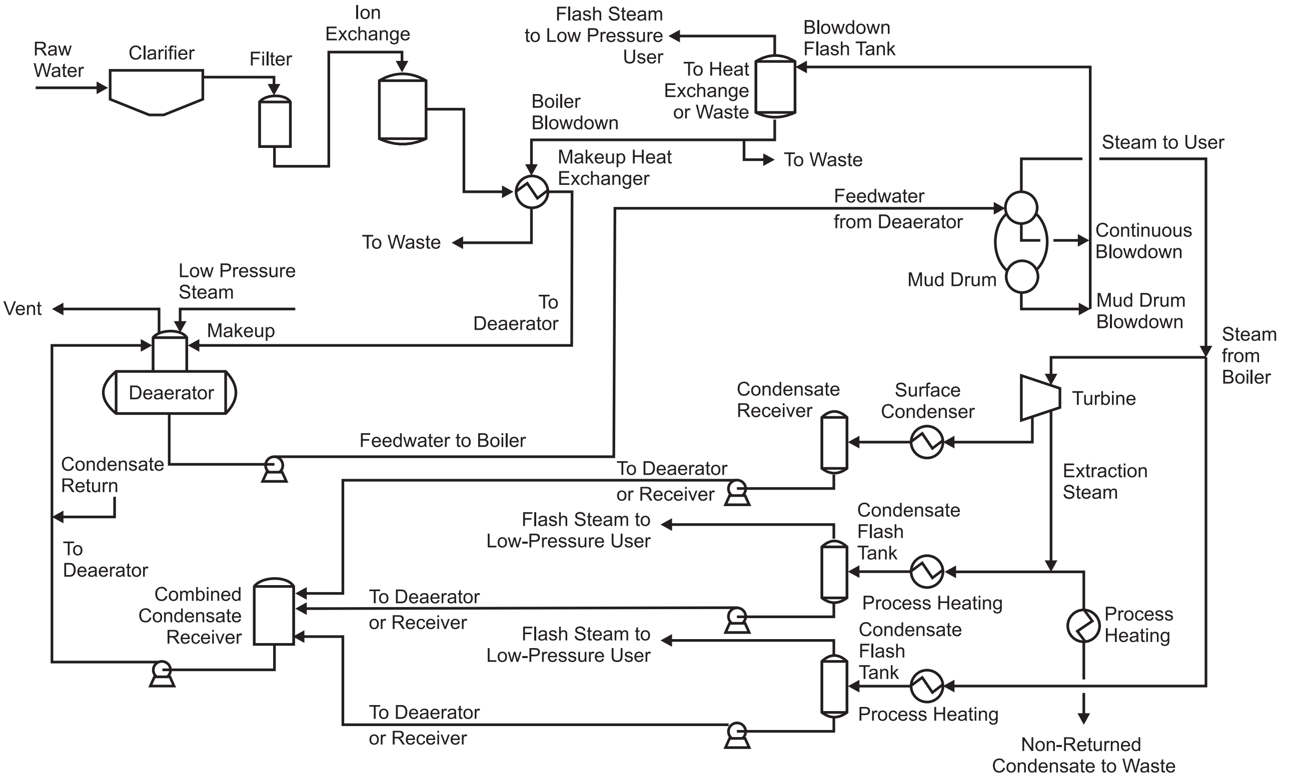


FIGURE 9.8 Typical industrial boiler system.

sample, leading to a low percent blowdown. Ideally, both the feedwater and boiler water samples should be neutralized, but this is rarely done.

The percent makeup can be calculated using the TDS in the feedwater, makeup, and condensate.

$$\%\mathrm{MU} = (100)(\mathrm{TDS}_{\mathrm{FW}} - \mathrm{TDS}_{C})/(\mathrm{TDS}_{\mathrm{MU}} - \mathrm{TDS}_{C}) \qquad (9.5)$$

where TDS_C = TDS in recovered steam condensate, mg/L
$\mathrm{TDS}_{\mathrm{MU}}$ = TDS in makeup, mg/L

Note that the above calculations do not apply to boilers using high-purity feedwater, because the TDS in the feedwater is too low to measure accurately. Chapter 33 on the Power Industry discusses alternate methods for these applications.

Cycles of Concentration

As discussed earlier, when steam (devoid of solids) is generated, dissolved solids remain behind and concentrate in the boiler water. Figure 9.9 shows that as water evaporates, remaining dissolved solids increase in concentration. The ratio of the quantity of dissolved solids in the boiler water to those in the feedwater is defined as the concentration ratio (CR) or cycles of concentration (COC). Expressed another way, the number of COC in a boiler system is simply the reciprocal of the percent blowdown.

$$\mathrm{COC} = 100/\%\mathrm{BD} \qquad (9.6)$$

There are times, such as when the makeup water is demineralized and contains little to no dissolved solids, when conductivity cannot be used to measure the COC. In these cases, some other method must be used to measure the COC. This can be done by

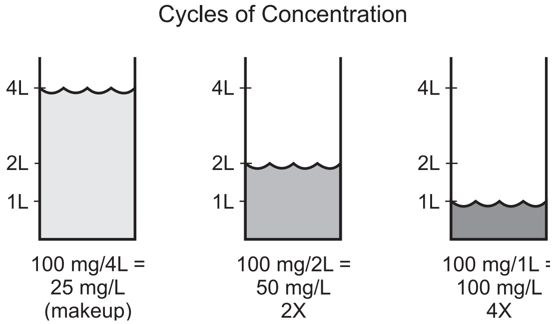


FIGURE 9.9 An illustration of increasing dissolved solids as water evaporates.

injecting into the feedwater a tracer that is nonvolatile, nonreacting, and nonprecipitating. By measuring the concentration of traced fluorescence chemistry in the feedwater and in the boiler water, the ratio of the boiler water concentration of the tracer chemistry to the concentration of tracer chemistry in the feedwater represents the COC.

$$\text{COC} = \text{BW concentration}/\text{FW concentration} \tag{9.7a}$$

If the boiler continuous blowdown and the steam flows are measured, the COC can be calculated using Eq. (9.7*b*).

$$\text{COC} = (S + \text{BD})/\text{BD} \tag{9.7b}$$

where S = steam mass flow, lb/h (kg/h)

Once the COC is known, the blowdown flow can be calculated from the following:

$$\text{BD} = S/(\text{COC} - 1) \tag{9.7c}$$

Likewise, the feedwater flow can be calculated using Eqs. 7*d* and 7*e*.

$$\text{FW} = S + \text{BD} \tag{9.7d}$$

$$\text{FW} = (S)(\text{COC})/(\text{COC} - 1) \tag{9.7e}$$

The blowdown flow can also be calculated from measurements of the steam flow and the feedwater flow, although this calculation will result in a higher error, because a relatively small number is calculated from the difference between two larger numbers, and these numbers are taken from two separate meters, both of which may be out of calibration.

$$\text{BD} = \text{FW} - S \tag{9.7f}$$

Mass Balance Equations

Figure 9.8 shows the boiler plus the three support systems: pretreatment, feedwater, and condensate systems. Simple mass balances describing these systems and their relationships are defined by the following equations.

$$\text{FW} = \text{MU} + \text{RC} + \text{DA} - V \tag{9.8}$$

$$S = \text{RC} + \text{NRC} \tag{9.9}$$

where RC = returned steam condensate mass flow, lb/h (kg/h)
DA = deaerator heating steam mass flow, lb/h (kg/h)
V = deaerator vent mass flow, lb/h (kg/h)
NRC = nonreturned steam condensate mass flow, lb/h (kg/h)
S = steam

An accurate water analysis plus one or two measured flow rates can be used to determine most other system flow rates. These, in turn, can be used to calculate chemical dosages, size equipment properly, and estimate the heat and energy content of various streams.

Many times, feedwater and makeup flow rates are not metered but steaming rate is. Knowing boiler water and feedwater chemical compositions will allow feedwater, makeup, and blowdown flow rates to be calculated.

Optimizing the Water Balance

Because boiler systems are energy intensive and the fuel needed to produce energy is expensive, it is in a plant's best interest to maximize steam production and minimize fuel consumption.

The first step in optimizing the system is to take every practical measure to eliminate steam and condensate losses, in addition to working within the economic constraints of the cost of revisions, new equipment, piping, and installation. For example, it might be practical to install piping to return condensate from a tank farm in a refinery or petrochemical plant, but if the condensate is badly contaminated with oil, the extra cost of installing and operating condensate filters may not be justified.

The next major step is to minimize blowdown, or to get the most mileage from the makeup for the control limits required by the boiler. Because the makeup treatment system is in place, a plant usually must do its best with the system at hand; in some cases, however, a new system may be required to optimize makeup use. Major unit operations of makeup treatment are discussed in Chap. 6 on Raw Water Clarification and Filtration, Chap. 7 on Ion Exchange, and Chap. 8 on Membrane Separation; all found in Sec. 3.1.

As shown in the ASME guidelines, the limits on such controls as total dissolved solids, silica, and alkalinity are related to the amount of these materials coming in with the makeup water. These concentrations are usually adjusted by blowdown, but some manipulation of the makeup treatment system might be possible, depending on system flexibility. Other constituents such as phosphate, organics, and sulfite are introduced as internal treatment chemicals, and their concentration can be adjusted by changing their rate of application.

Table 9.1 illustrates how minimizing boiler blowdown can optimize a boiler system. Consider a 600 psig (4.1 MPag) boiler system in a paper mill. The makeup is treated by hot lime softening followed by ion exchange softening, and after treatment has a total dissolved solids concentration of 150 mg/L and a silica concentration of 3 mg/L. The makeup rate is 50% based on the feedwater flow.

Using 50% condensate return, this example will yield a feedwater TDS and silica of 75 mg/L and 1.5 mg/L, respectively. With an

Factor	Makeup	Feedwater	Limit	Maximum Boiler Concentration Ratio
TDS, mg/L	150	75	2000	26.7
SiO_2, mg/L	3	1.5	30	20.0
SiO_2, mg/L (after reduction)	2	1.0	30	30

Table 9.1 Maximum Concentration Ratio

allowable limit of only 30 mg/L silica in the boiler, silica is the controlling factor that sets the maximum CR at 20 (5% blowdown). The water could be concentrated by a factor of 26.7, however, based on total dissolved solids, so there is incentive for additional silica reduction in the treatment unit. The addition of dolomitic lime (rather than hydrated lime) or the addition of magnesium oxide in the hot lime softener, might permit a reduction from 3 mg/L to less than 2 mg/L silica in the makeup. With lower silica in the makeup, silica in the feedwater will be reduced accordingly.

Reducing silica in the makeup from 3 to 2 mg/L will reduce it equivalently in the feedwater. Therefore, the feedwater would then contain only 1 mg/L silica, and blowdown based on silica could potentially be reduced to 1/30 or 3.3%. Now, the limiting factor would no longer be silica but total dissolved solids. The boiler may now be cycled up to its maximum for conductivity at 26.7 cycles or 3.75% blowdown. Depending upon steam production, the availability of blowdown heat recovery equipment, and fuel costs, the additional 25% blowdown reduction (5–3.75% blowdown) could result in sizeable fuel savings for fired boilers. There will be additional savings in reduced makeup water costs and blowdown sewer costs.

This example shows that the CRs are determined easily by chemical analysis. Blowdown rate is rarely metered, although most plants meter makeup, and some meter feedwater as well. Steam flow is usually metered in most plants, and the feedwater flow can be calculated based on the CR and the steam production by using the mathematical relationships discussed previously.

Thermodynamic Properties of Steam

Steam and water at different pressures and temperatures contain different amounts of energy. The difference between the energy content of steam and water at the same pressure and temperature is significant and represents the driving force of the steam. The thermodynamic properties of saturated steam and water are shown in saturated steam tables, which are available in numerous reference books and on the internet.

Terminology

The concepts of work and energy are important to understand how steam can be utilized in a wide variety of applications. Following are terms commonly used for defining energy, work, and power.

Work: The product of a force (F) applied uniformly along or through a distance (d) is defined as work. For example, the work expended in lifting a weight requiring an applied force (F) where the distance (d) in transit is upward is calculated as follows:

$$\text{Work} = (\text{force})(\text{distance})$$

Work is expressed in ft · lb or kg · m

Heat: The amount of energy given up or absorbed by a substance is equal to the product of the mass of a substance (m) heated uniformly, its temperature change (ΔT), and its specific heat (C_p), which is a function of the nature of the substance heated (for water, C_p = 1 Btu/lb, 1 kcal/kg, or 4.184 kJ/kg).

$$\text{Heat} = mC_p\Delta T$$

Heat is expressed in Btu, kcal, or kJ

Heat equivalent of work: A Btu is defined as the amount of heat necessary to raise the temperature of 1 lb of water 1°F. Also, 1 Btu = 777.6487 ft · lb. A kilocalorie is defined as the amount of heat necessary to raise the temperature of 1 kg of water 1°C, and 1 kcal equals 4.184 kJ. Also, 1 J = 0.102 kg · m.

Electrical equivalent of work: The unit of electrical energy is the kilowatt-hour (kWh). The mechanical energy of an engine driving an electrical generator is converted to electrical energy. Common units of energy include Btu, ft · lb, kg · m, kWh, kcal, and kJ.

$$1\ \text{kWh} = 3414.426\ \text{Btu} = 2\,655\,224\ \text{ft}\cdot\text{lb}$$

$$1\ \text{kWh} = 860.42\ \text{kcal} = 3600\ \text{kJ} = 367\,098\ \text{kg}\cdot\text{m}$$

This is the most commonly misunderstood energy relationship, because kilowatts are often erroneously considered an energy term rather than a power term.

Power: This is the rate or speed of doing work, generating heat, or producing electricity. For example, a person weighing 150 lb (68 kg) and climbing a 100 ft (30.5 m) hill would expend 15 000 ft · lb (2074 kg · m) of energy. If this climb requires 10 minutes (600 seconds), the energy expended would be 25 ft · lb/s (3.46 kg · m/s). The power applied is defined as:

$$25\ \text{ft}\cdot\text{lb/s}/[550\ (\text{ft}\cdot\text{lb/s})/\text{hp}] = 0.045\ \text{hp}$$

$$3.46\ \text{kg}\cdot\text{m/s}/[76\ (\text{kg}\cdot\text{m/s})/\text{hp}] = 0.045\ \text{hp}$$

If the hill is climbed in five minutes, 15 000 ft·lb (2074 kg·m) of energy are still used, but the power exerted is doubled.

$$15\ 000\ \text{ft}\cdot\text{lb}/300\ \text{s}/(550\ [\text{ft}\cdot\text{lb/s}]/\text{hp}) = 0.09\ \text{hp}$$

$$2074\ \text{kg}\cdot\text{m}/300\ \text{s}/(76\ [\text{kg}\cdot\text{m/s}]/\text{hp}) = 0.09\ \text{hp}$$

Common units of power include hp, kW, Btu/h, kcal/h, and kJ/h.

$$1\ \text{hp} = 550\ \text{ft}\cdot\text{lb/s} = 0.7457\ \text{kW} = 2546.137\ \text{Btu/h}$$

$$1\ \text{hp} = 76\ \text{kg}\cdot\text{m/s} = 641.62\ \text{kcal/h} = 2684.52\ \text{kJ/h}$$

Boilers

The primary purpose of chemical treatment is to protect the generating system from such problems as scale, corrosion, and carryover. When these problems occur, production efficiency decreases, maintenance requirements and costs increase, and overall plant productivity decreases.

The proper application of chemical technology requires a thorough understanding of the systems to be treated. Each piece of equipment, be it a boiler, a turbine, a superheater, or a condenser, has its own requirements. Special care must be taken that each piece of equipment in a system be compatible with the overall system and with the treatment program selected.

It is not enough that each element of the heat-generating unit be efficient and well-constructed. In today’s economy, the unit must provide the anticipated maximum overall efficiency and reliability at minimum cost. To achieve this goal, the unit and all auxiliary components must comprise a balanced, well-designed system.

The following requirements must be considered when selecting equipment:

- Adequate strength of all components
- Satisfactory service life
- Adequate expansion capabilities
- Accessibility of all parts for inspection
- Readily available replacement parts
- Safety and reliability
- Overall energy integration and utilization

Plants frequently sacrifice one or more of these considerations in favor of low cost. This sacrifice may eventually result in operational and control problems after the unit is installed.

Plants and engineering companies often call upon water treatment chemical suppliers to work with them in the design stages and recommend the best treatment program for the new system. Such input can help the plant avoid costly mistakes that could result in serious operating problems once the boiler is online. Careful input, based on a strong knowledge and understanding of the equipment and of the equipment selection process, will mean fewer problems once the boiler is operational.

Boiler Classifications

Boilers today may be classified on the basis of any number of the following characteristics:

- Use
- Pressure
- Orientation
- Materials of construction
- Size
- Tube contents
- Firing
- Heat source
- Circulation

A general understanding of these classifications will promote better owner-supplier understanding and communication.

Use: Boilers are normally classified by the particular service they are to perform. Customarily, boilers are classified as either stationary or mobile (mainly marine) units. Stationary boilers may be used for building heat, plant process steam, power generation, or waste heat removal. Mobile boilers can serve all of the purposes that stationary boilers serve; however, their location will not be permanently fixed.

Pressure: The ASME boiler code differentiates boilers based on the following pressure differences:

- Low-pressure units are all steam boilers that do not exceed pressures of 15 psig (103 kPag), and all hot water boilers that do not exceed 160 psig (1.1 MPag) and 250°F (121°C).
- Power boilers are all boilers that exceed the low-pressure limits.

Orientation: Looking at the boiler from the burner side, the front of the boiler is the side of the boiler where the burner(s) is/are located; the back of the boiler is the side opposite the burner(s); the left side of the boiler is to the left, and the right side of the boiler is to the right. Some boilers, such as opposed-wall fired and tangentially fired, do not adhere to this typical convention.

Materials of construction: Boilers are normally constructed of steel or cast iron. Steel boilers are more common, consisting of steel plates and tubes joined together by riveting, welding, or rolling. Cast iron boilers are constructed of gray iron casting connected by push-in nipples.

Size: Boilers are rated in heating surface available and heat input per hour that they can tolerate. Industrial boilers are normally considered to have a heating surface greater than 294 ft^2 (27.3 m^2); residential units have heating surfaces of 16 to 294 ft^2 (1.5–27.3 m^2).

Tube contents: Boilers classified by tube contents consist of two types: watertube boilers and firetube boilers. Firetube boilers are those in which the tubes are surrounded by water, and the hot gases pass through the tubes. Watertube boilers are those in which water flows through the inside of the tube, and the hot gases are on the outside.

Firing: Boilers may be classified as either fired or unfired. In fired boilers, the heat supplied to generate steam is a direct result of burning fuel. Unfired boilers are units that use waste heat to generate steam; there is no direct burning of fuel.

Heat source: The heat to warm the water and generate steam may be derived from the following sources:

- Combustion of solid, liquid, or gaseous fuels
- Hot gases from chemical reactions
- Electrical energy
- Nuclear energy

Circulation: Boilers classified by circulation patterns include natural, positive (or forced), and once-through. Each of these classes will be discussed under Boiler Circulation later.

Boiler Types

Steel boilers are by far the most common type of boiler constructed today. These boilers are constructed as either firetube or watertube units.

Firetube Boilers

The original shell boiler (tea-kettle type) was first improved upon by passing the hot gases through the inside of tubes located within a shell filled with water. This modification marked the beginning of the firetube boiler as we know it today.

Firetube boilers are used principally for heating systems, for industrial process steam, and as portable steam-generating units. These boilers operate at pressures up to 600 psig (4.1 MPag) and steam flows up to 40 000 lb/h (18 000 kg/h). The firetube unit is best suited for a plant where steam demands are relatively small, and no turbine applications require superheated steam.

The firetube units have the advantage of large water storage capacity and the ability to partially dampen the effect of wide and sudden load swings in steam demand. Because of their large water volume, however, the time required to arrive at operating pressure from a cold start is considerably longer than for a watertube boiler.

The shells of firetube boilers are normally cylindrical, with the tubes set into tube sheets. This type of construction is particularly adaptable to boilers operating at 250 psig (1.7 MPag) or less. The steam boiler water line is normally more than 2.5 inches (63.5 mm) above the top of the upper rows of tubes or crown sheet. The space above the water line is called the steam space.

Tubes normally measure 2 to 4 inches (51–102 mm) in diameter. The boiler may have one, two, three, and occasionally four gas passes, a pass being a group of tubes through which the combustion products flow in essentially one direction. Three-dimensional cutaway views of firetube boilers are shown in Figs. 9.10 to 9.12.

In most firetube boilers, the burner is located at the front end of the boiler in the combustion chamber, which is a large diameter tube running the length of the unit. The hot gases from combustion

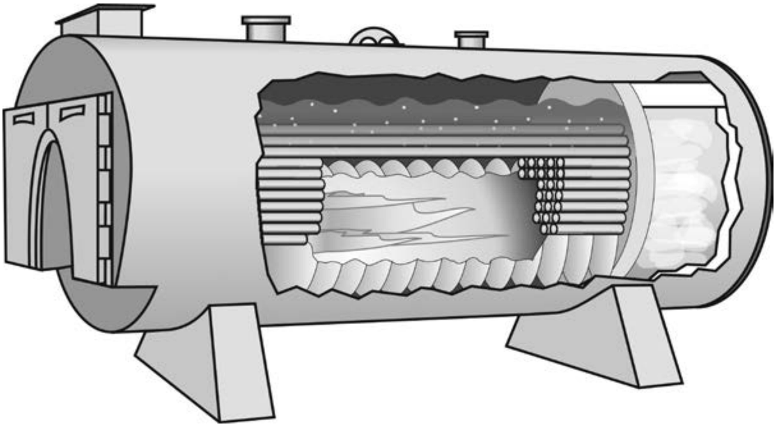


Figure 9.10 Scotch-type boiler. Combustion occurs in the corrugated internal furnace; refractory-lined rear chamber reverses flow and directs gas forward through tubes to outlet at front.

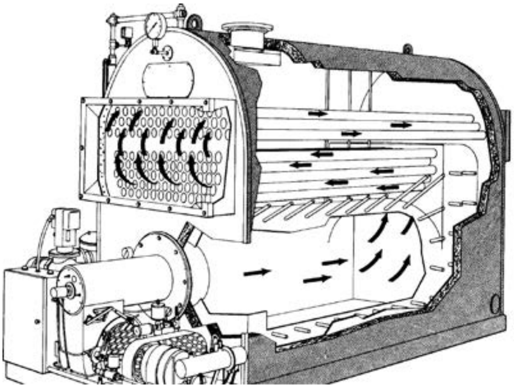


Figure 9.11 Large firebox-type unit. Direction of gas flow is forward in the short second-pass tubes and to the rear in the longer third-pass tubes.

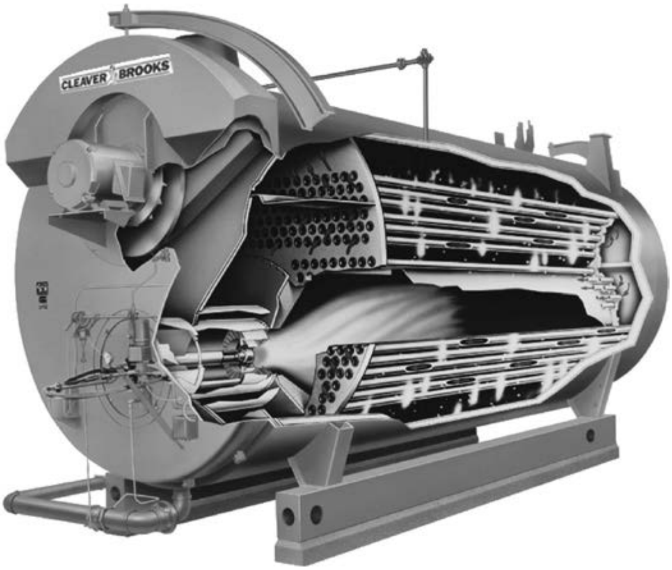


Figure 9.12 For maximum travel of hot gas and high efficiency, the four-pass design is used. In this boiler, gas velocity is maintained by a decrease in the number of tubes to give each succeeding pass a smaller cross-sectional area. (*Courtesy of Cleaver Brooks, Inc.*)

travel down the combustion chamber to the back end of the boiler where the gases are directed, by baffles, toward the front of the unit through the smaller diameter tubes. In multipass units, the hot gases are redirected back toward the rear of the unit, again with the use of baffles.

Watertube Boilers

A watertube boiler is composed of drums, headers, and tubes. The water and steam are contained within the tubes, while the heat is applied outside the tubes. The tubes, through which the water circulates and in which steam is generated, are outside the drums. Because the water drums are used for storage of water and steam, they are not required to contain any tubular heating surface. Most watertube boilers have natural circulation; however, some forced (positive) circulating units are in use.

Watertube boilers may be of the straight-tube or bent-tube type. The various bent-tube boilers, with higher pressures and temperatures, have gradually replaced the horizontal straight-tube units.

The initial cost of a watertube boiler is higher than that of an equivalent firetube boiler. The cost of a firetube boiler is commonly said to be half of the cost of an equal steaming rate watertube boiler. The higher efficiency of watertube boilers will, however, eventually offset higher initial capital cost. Additions of economizers, superheaters, and reheaters will permit recovery of initial capital cost even more quickly.

Horizontal Straight-Tube Boilers Modern, more efficient boilers are largely replacing the horizontal straight-tube boilers of the early 1900s. Some of these older units, however, are still operational, and a brief discussion is appropriate. Horizontal straight-tube boilers cover a wide range of capacities and pressures. They are used primarily to generate process steam and occasionally to generate building heat and power.

The horizontal units are limited to an hourly production of 10 000 lb of steam per foot of boiler width (14 900 kg/m). The unit is usually field erected. These boilers had early and persistent popularity because of favorable manufacturing and erection costs plus their adaptability to many uses.

These units are not without their drawbacks, however:

- Access into these units involves considerable downtime.
- Limited steam separating ability makes adequate separation at higher steaming rates difficult, if not impossible.
- Steaming rates are sharply limited by relatively low circulation rates and poor water distribution.

The straight-tube boiler is made up of a bank of tubes that are inclined and staggered. The tubes are inclined at an angle of 5 to 15° to promote circulation.

The header provides a flat surface for tube connections. It may be connected to the drum by means of circulation tubes (risers and downcomers) or by sheet steel saddles. The drum may be either longitudinal (parallel to the tubes), or it may be across (perpendicular to the tubes).

Boiler manufacturers varied the heating surface area (corresponding boiler capacity) by changing the tube length and number of tube rows in both height and width. For higher pressures, the header design was changed and required greater tube spacing and tubes of a smaller diameter.

Superheaters may be installed on straight-tube units with a maximum temperature rise of about 100°F (38°C). They are normally called over deck or inter deck, depending upon where they are installed.

The steam and water move along the inclined tubes to the front. The water then flows through the headers and into the steam drum. The cooler water flows down the downcomer to the rear header and finally into the generating tubes to complete the circulation cycle.

Bent-Tube Boilers The common bent-tube boiler offers many advantages over the straight-tube units, such as:

- Great economies in fabrication and operation because of the use of welding, improved steels, water-wall construction, and new manufacturing techniques
- Greater accessibility for cleaning and maintenance
- Ability to operate at higher steaming rates and produce a better quality of steam

The main elements of the bent-tube boiler are essentially drums connected by bent tubes (Fig. 9.13). With a water-cooled furnace, bent tubes are arranged to form the furnace enclosure. Most modern boilers, from small packaged boilers to large utility stations, are of this general design.

The early bent-tube units were of the four-drum design. Although the four-drum design is sound, improvements permitted the trending toward three- and later two-drum units. The smaller bent-tube units (packaged boilers) of today have been standardized to three basic designs. Popular packaged boiler designs are the two-drum "O" type and "D" type units as well as the three-drum "A" frame unit (see Figs. 9.14–9.16).

As furnace size and temperatures increased, refractory maintenance became excessive, particularly when firing with coal in field-erected units. The higher gas temperatures caused increased slagging of the boiler surfaces. Furnaces today are normally completely water cooled (water-wall tubes) to overcome short refractory life and excessive fireside temperatures due to slagging. An additional advantage of water-wall tubes is that they are also steam generators, an aid in obtaining higher steaming capacity.

In Figs. 9.14 to 9.16, water enters the main steam drum and flows down the downcomers to the mud drum, then up the steamer

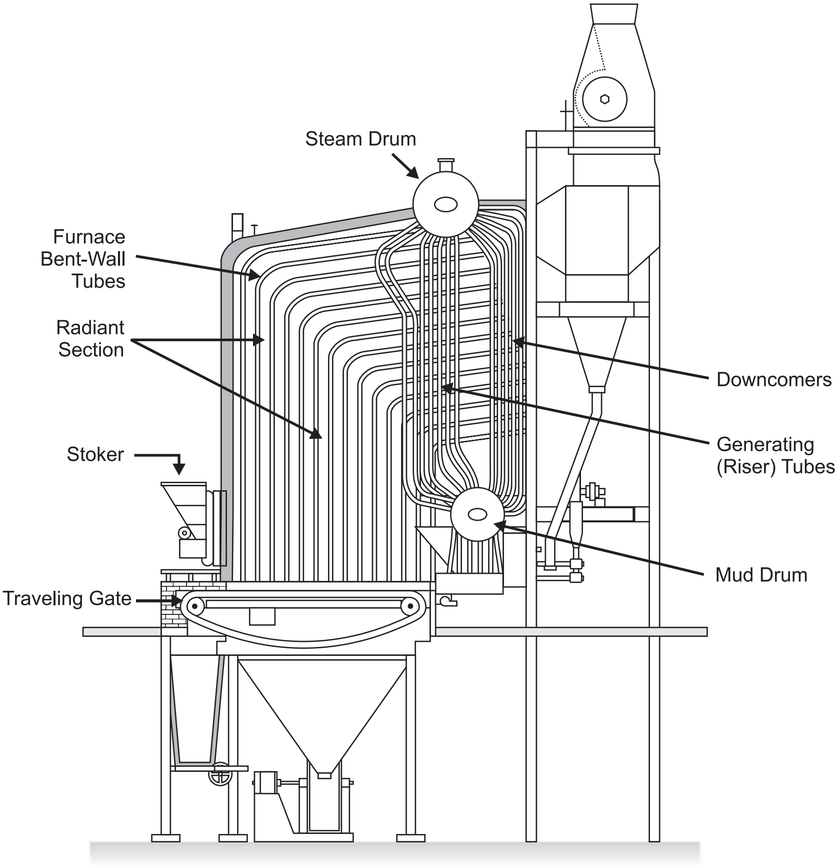


Figure 9.13 Bent watertube boiler.

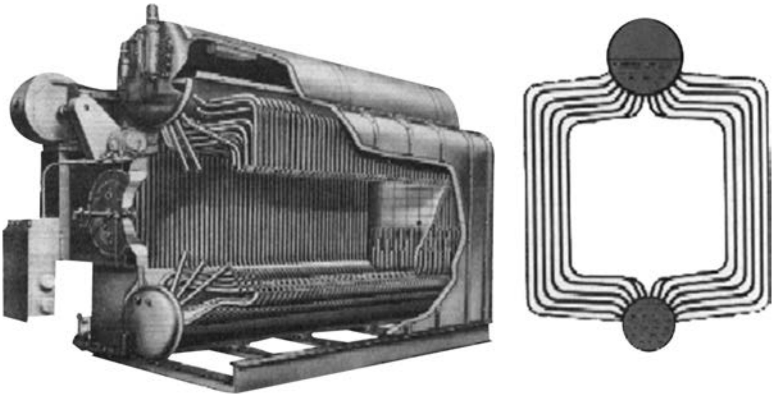


Figure 9.14 O-type packaged watertube boiler. Transportation limits the height of the furnace; for higher capacity, a longer boiler is required.

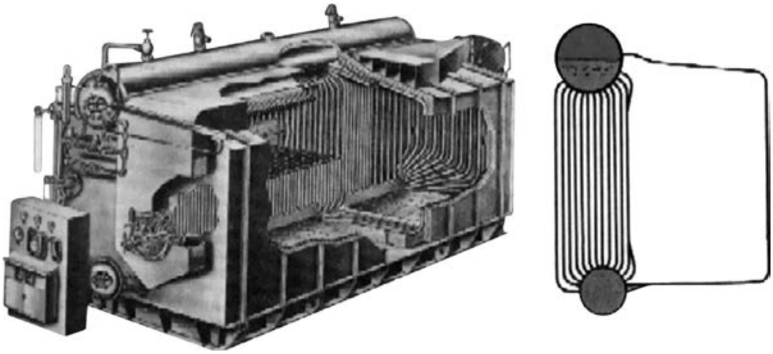


Figure 9.15 D-type packaged watertube boiler. Burners may be located in one-end wall.

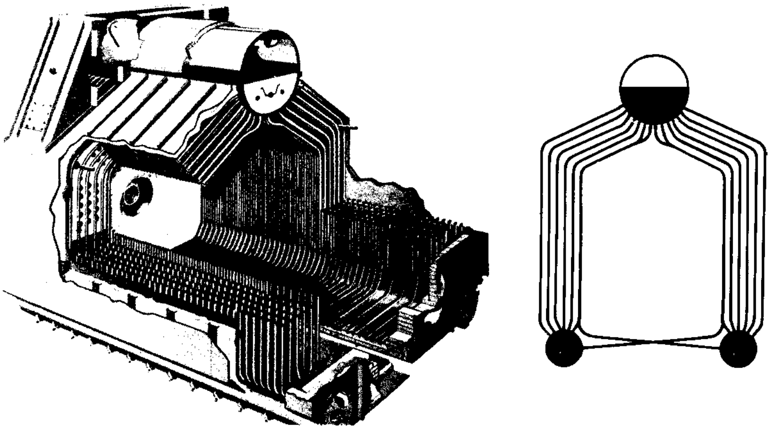


Figure 9.16 A-type packaged watertube boiler. The upper drum is larger to permit separation of steam and water.

or riser tubes and back to the steam drum. For a more detailed explanation of boiler circulation, see Boiler Circulation later in this chapter.

Cast Iron Boilers

Cast iron boilers are used primarily for low-pressure heating system applications. They generate 15 psig (103 kPag) steam or 30 psig (207 kPag) hot water. Cast iron boilers are usually designed in sections. These sectional castings are connected together by push-in nipples, and the whole unit is held together by tie rods or bolts.

Waste Heat Boilers

Heat recovery from industrial waste products or gases is often necessary from an economic, process requirement, or pollution standpoint. All or part of the steam requirements of a plant may be supplied by waste heat boilers. This section presents only a brief overview of the many types of waste heat boilers in use today.

Heat may be recovered from any number of sources, such as:

- Heat that originated as a necessary part of the process and would otherwise be discarded, for example, ammonia reformer, open-hearth furnaces, basic oxygen furnaces, gas turbine exhaust, etc.
- Heat that is a by-product of a chemical reaction process, for example, black liquor recovery boilers.
- Heat that is available from burning wastes, for example, waste wood, organic waste, garbage, or carbon monoxide (CO) gas in a refinery. In one respect, these could be considered fired boilers, but in another respect, they could be considered waste heat boilers. For example, the main purpose of a garbage incinerator is to burn garbage, and the heat generated can be considered waste heat.

Wherever a process waste product or gas is discharged at a temperature of 1000°F (538°C) or higher, heat recovery should be considered. Table 9.2 illustrates the temperature of various waste heat gases that can be used to heat boilers.

The selection of a waste heat boiler is based upon many of the following considerations:

- Chemical nature, temperature, and corrosivity of the gases
- Quantity, amount, and nature of the dust contamination
- Available draft
- Desirable location for the flue outlet
- Whether the gases are under pressure or suction
- Available space
- Requirements for supplemental firing for start-up, preheating, emergency use, stabilizing furnace conditions, or added capacity
- Other special requirements of the individual process

In general, to offset the lower gas temperatures available in a waste heat system, design considerations are made to provide for a relatively high gas velocity over a small number of tubes to increase the convection heat transfer. Mass flows of 6000 to 8000 $\mathrm{lb/[h \cdot ft^2]}$

Source of Gas	**Temperature**	
	°F	**°C**
Ammonia oxidation process	1350–1475	730–800
Annealing furnace	1100–2000	590–1090
Black liquor recovery furnace	1800–2000	980–1090
Cement kiln (dry process)	1150–1350	620–730
Cement kiln (wet process)	800–1100	430–590
Coke oven beehive	1950–2300	1070–1260
Coke oven by–product	Up to 750	Up to 400
Copper refining furnace	2700–2800	1480–1540
Copper reverberatory furnace	2000–2500	1090–1370
Diesel engine exhaust	550–1200	290–650
Forge and billet heating furnace	1700–2200	930–1200
Garbage incinerator	1550–2000	840–1090
Gas benches	1050–1150	570–620
Glass tanks	800–1000	430–540
Heating furnace	1700–1900	930–1040
Malleable iron air furnace	2600	1430
Nickel refining furnace	2500–3000	1370–1650
Open hearth steel furnace		
• Producer gas-fire	1200–1300	650–700
• Oil, tar, or natural gas	800–1100	430–590
Petroleum refinery still	1000–1100	540–590
Sulfur ore processing	1600–1900	870–1040
Zinc fuming furnace	1800–2000	928–1090

Table 9.2 Temperature of Waste Heat Gases

[29 000–39 000 kg/(h·m^2)] of gas are common today. An average gas velocity of 40 to 50 ft/s (12–15 m/s) is used at gas temperatures of 1300°F (704°C).

Boiler capacity is limited by the maximum allowable draft loss; heat efficiencies of 60 to 70% can still be obtained by using economizers.

Specific process requirements in the production of steel, paper, ammonia, and other products have resulted in the design of various types of waste heat boilers. Two common designs today are the gas-tube unit for gas streams containing contaminants that could cause fouling, and the watertube unit for clean gases.

Gas-Tube Waste Heat Boilers A direct-fired, firetube boiler that has part of its shell exposed to the furnace absorbs heat by both radiation and convection, thus making more efficient use of its surfaces. Gas-tube waste heat boilers, however, usually have just a single-pass arrangement that absorbs only convection heat from the gases. These gas-tube units have a high weight-to-heat output ratio because the exterior shell is not used as a heating surface. Gas-tube boilers of this type are most suitable for pressures around 400 to 500 psig (2.8–3.4 MPag) and gas temperatures as high as 1800°F (982°C).

Tubes of these units are of smaller diameter and more closely spaced than tubes in watertube waste heat units. The tubes are kept clean of deposits by a rotating arm soot blower with nozzles directed toward the tube ends. These boilers are designed to handle only light dust loading (gas particulates) and should not be used where dust loading of the gas is greater than 0.5 g/ft^3 (17.7 g/m^3).

Gas-tube units may be either horizontal or vertical in design. In horizontal units, practically the entire space within the shell is filled with tubes (Fig. 9.17). The steam space is minimized; instead, a separate steam drum may be used. The boiler may be set at an angle of 15° to improve circulation, provide for steam collection at the highest point, and permit suspended matter to move to the lowest point. Vertical units are very similar to horizontal units except the gas tubes are vertical.

Watertube Waste Heat Units The major considerations in the design of a watertube unit are the cooling of sticky particles before their entry into the convection section and the problems caused by high dust loading.

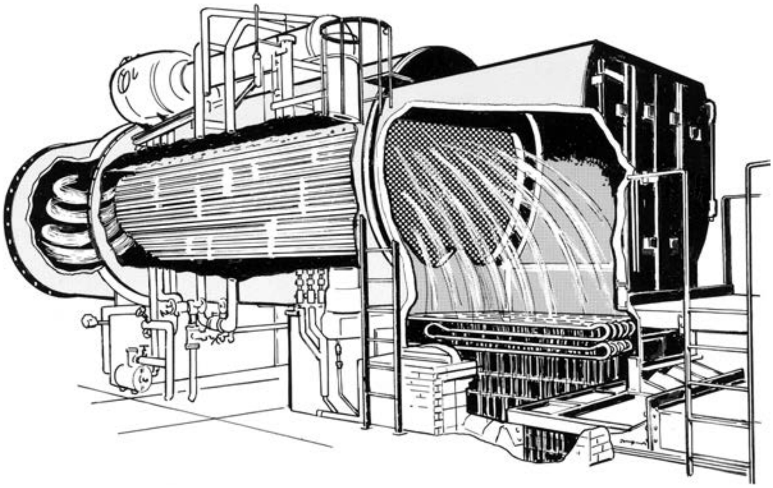


Figure 9.17 Gas-tube waste heat boiler.

Watertube waste heat units are more widely used than gas-tube waste heat boilers for the following reasons:

- Dust may be recovered and collected.
- Tube sizing and spacing may be varied to prevent slagging.
- Damage due to gas temperature fluctuations is minimized.
- The waterside is easier to treat and keep clean.
- More economical design arrangements are possible.

Applications of Waste Heat Boilers Open hearth, forge, and continuous heating furnaces in steel mills are usually equipped with waste heat boilers. Coke oven gas and blast furnace gases are normally used as the heat source for the waste heat units. Much of the steam generated in refineries and petrochemical and chemical plants is of the waste heat type. Ammonia plants, for example, generate steam via waste heat units by cooling the synthesis gas from the reforming furnaces. In the case of ammonia plants, approximately 95% of the steam on-site is generated by waste heat. In the Kellogg-type ammonia plants, the main waste heat boilers are bayonet tube/scabbard design, where other ammonia plant designs might use vertical shell-and-tube designs. Waste heat units such as bayonet, TLX (transfer line exchanger), and numerous other types are found more often in plants where process temperature control and energy conservation are of prime concern.

Ore roasters and cement kilns: A three-drum, low-head, watertube, waste heat boiler is used to recover heat from the ore roasters and kilns.

Lead and zinc smelters: After the lead and zinc are boiled out from the slag, they are reoxidized in a fuming furnace. Gaseous products from the fuming furnace have temperatures of 2200°F (1200°C) and are passed through a watertube waste heat boiler to cool them down to 1400°F (760°C).

Papermaking: In the manufacture of paper, wood is cooked in digesters with live steam, sodium hydroxide, and sodium sulfite. The liquid waste from these cookers contains lignin and reacted chemicals. A recovery unit (black liquor boiler) is used to recover the chemicals (salt cake), generate process steam by burning the waste liquor, and eliminate waste to meet pollution requirements. During the burning of black liquor, the recovered salts are molten, and this smelt accumulates in the bottom of the boiler, where it is decanted into the dissolving tank. The recovered green liquor is then reused in the process. If a tube leak should occur in these boilers, the water from the leak will react with the molten salt, potentially resulting in a violent explosion.

> *Petroleum industry*: In the petroleum industry, the efficient operation of a fluid catalytic cracking unit produces gases rich in carbon monoxide (CO). To reclaim the thermal energy represented by these gases, the cracking units are designed to include a CO boiler that uses this carbon monoxide as the fuel source to generate steam.

The operation of the CO boiler (Fig. 9.18) is coordinated with that of the catalytic cracker. Normally, the boiler is required to supply steam for the operation of the cracking unit and is started using supplementary fuel, for example, natural gas. Once the furnace temperature reaches approximately 1800°F (982°C), the CO gas is admitted to the furnace, and the supplemental fuel is reduced.

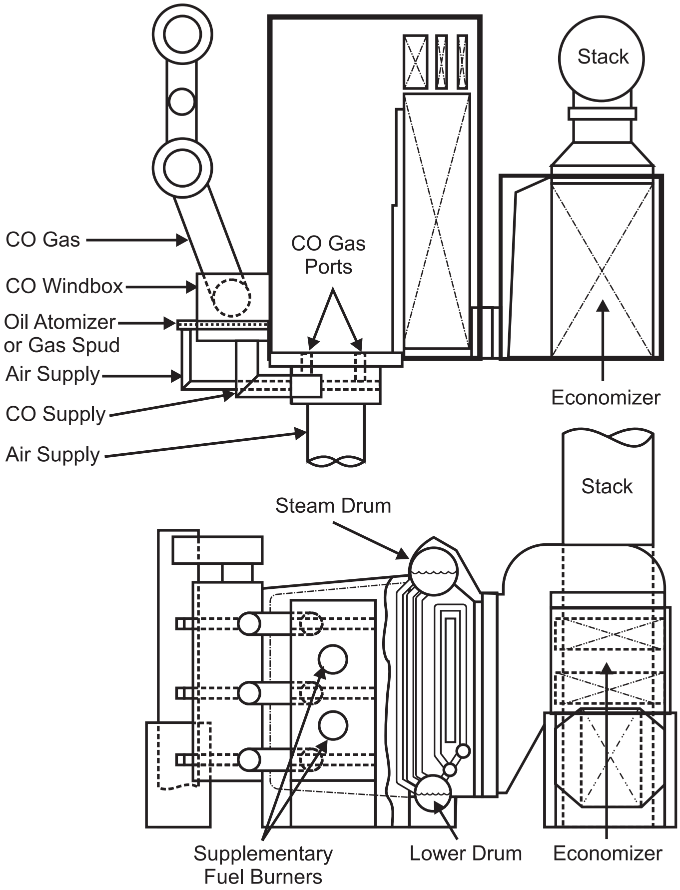


Figure 9.18 CO boiler illustration.

Coil Boilers

Coil boilers, or steam generators as they are commonly called, have become popular since the 1980s in medium industrial and institutional accounts for several reasons:

- Low water volume to boiler output
- Small footprint
- Quick steaming capability
- Skilled operators not required

While these boilers provide customers with the advantages presented above, they pose some interesting and unique treatment challenges.

There are two main design differences between boilers that fall into this category. The differences are in how steam and water are separated. One design (Fig. 9.19) utilizes a conventional steam drum to allow for the separation of steam and water, while the other design (Fig. 9.20) utilizes a steam separator and a trap to allow for steam/water separation. The coil orientation in the conventional design is horizontal, while the orientation in the steam separator system is vertical.

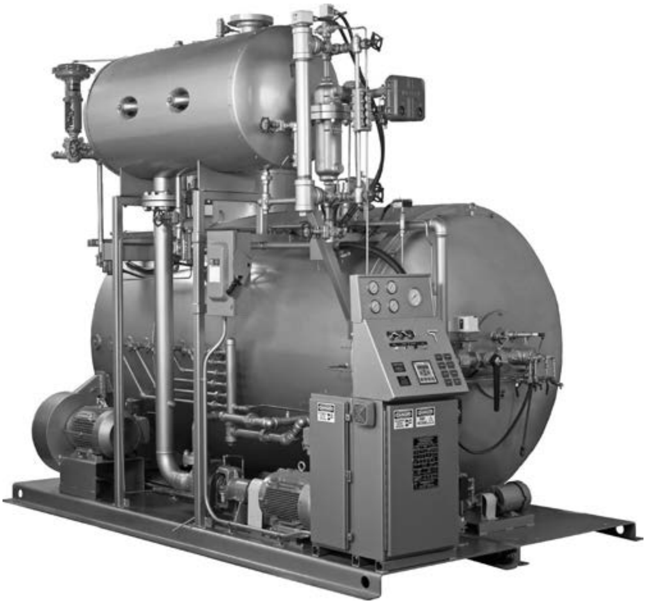


FIGURE 9.19 Photograph of a typical coil tube boiler with a conventional steam drum for steam/water separation. (*Courtesy of Thermogenics Inc.*)

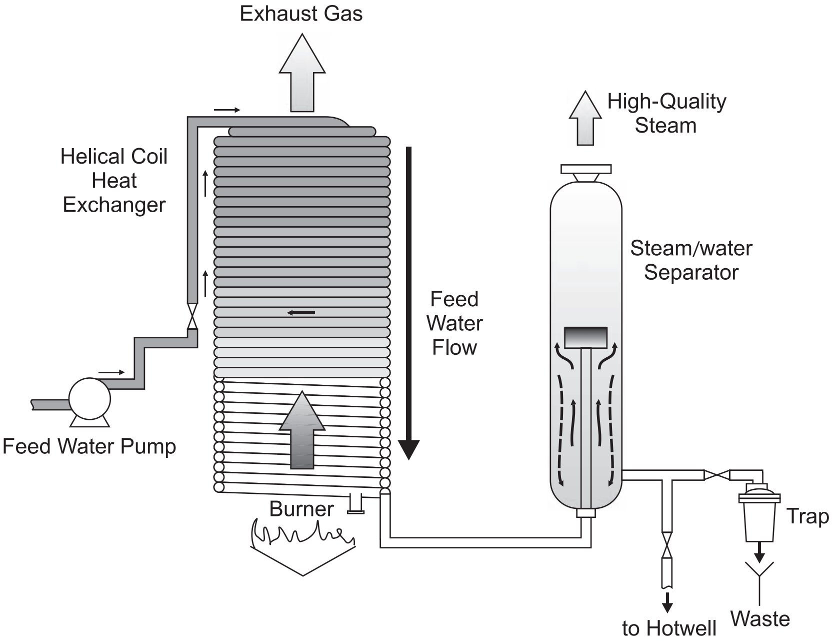


Figure 9.20 Schematic of a typical coil design boiler with a steam separator and trap system for steam/water separation.

Design differences notwithstanding, there are a few characteristics that are common in all coil steam generators:

- Maximum operating pressure of 250 psig (1.7 MPag)
- Boiler power range from 20 to 600 hp (14.9–447 kW)
- Water holding capacity range is 0.12 to 0.25 gal/hp (0.61–1.3 L/kW)
- Feedwater to steaming rate ratio of 1.1 to 1.25

Operation Despite the common characteristics, the ways water and steam are separated govern how these steam generators work. The steam generators with conventional steam drum operation (Fig. 9.19) operate on conventional methods of feedwater supply. That is, the feedwater demand is controlled by the steam drum water level. These units are, therefore, suitable to be integrated into a conventional firetube or watertube steam plant.

The steam generators that have a steam separator and trap system for steam/water separation (Fig. 9.20) recycle a portion of the boiler water back to the feedwater system and, therefore, are generally considered unsuitable for integration into an existing steam plant that has conventional firetube or watertube boilers. These steam generators need a stand-alone feedwater system.

Steam Separation with Drum In a coil boiler with steam drum separation (Fig. 9.19), there is a forced recirculation pump that pulls boiler water from the steam drum and sends it to a manifold that feeds several horizontal coils. These coils are designed in such a manner that they remain flooded at all times, with a steam/water mixture suitable for coil cooling. Each coil has a thermocouple to provide coil temperature data. The temperature on each coil should be closely monitored and is typically within 30 to 40°F (17–22°C) of the steam saturation temperature. Coils that exhibit a trend toward higher temperatures are typically not being cooled sufficiently and generally indicate deposition is occurring on the coil.

The steam/water mixture exits each coil and is gathered in a manifold and returned to the steam drum through a steam lance that is the primary steam separation vehicle. Secondary separation may be accomplished through baffling or screens. Blowdown is accomplished via a surface skimmer and conductivity control. Clean feedwater is fed into the steam drum to maintain a consistent water level in the drum from a conventional deaeration or atmospheric hotwell system.

Steam Separation with Separator and Trap In a coil boiler that utilizes a steam separator and trap system (Fig. 9.20), a feedwater pump feeds from an atmospheric hotwell or deaerator to the top of a vertical coil. This coil has three distinct sections:

1. Economizer pancake coil
2. Intermediate heating coil
3. Water-wall coil

The feedwater enters the economizer pancake coil at the top of the generator and travels counter-current to the flue gas. This coil is small in diameter with many winds. It transitions to the intermediate heating coil that has fewer winds and is larger in diameter. The final water-wall coil is single wound and larger again in diameter. A thermocouple is located in the water-wall coil. The steam/water mixture exits the base of the water-wall coil and is directed to a steam separator. The separated boiler water accumulates in the bottom of the separator and is trapped via an inverted bucket trap and directed back to the feedwater system for recycle. A proportioning valve is installed on the trap discharge that allows for some system blowdown each time the trap discharges.

The inverted bucket-trapping rate is governed by feedwater temperature. The trapping rate is usually set at 4 to 6 times per hour for systems where feedwater temperature is between 180 to 190°F (82–88°C). Systems with higher feedwater temperatures, such as those expected from a deaerated system at 250 to 350°F (121–177°C), have trapping rates of 10 to 15 times per hour. Since the discharge from the trap is recycled back to the deaerator or atmospheric hotwell, the calculation for cycles of concentration in this type of system must take into account the contribution of dissolved solids from this source. Hence, this type of system is designed to run between 4 to 5 COC of this less pure feedwater.

System Challenges While there are advantages in using a coil boiler, there are also challenges in keeping them running. Both of these systems are prone to specific difficulties that are treated a bit differently than a conventional watertube or firetube boiler. The common problem areas on these systems come from design, operation, and chemistry perspectives. Approaching system issue evaluation from the mechanical, operational, and chemical perspective generally yields good troubleshooting results. While each system is unique in design and operation, a number of the common problems are discussed below.

Oxygen Attack Coil boilers are very prone to failure from oxygen corrosion. They are usually treated with higher levels of oxygen scavenger to minimize this failure mechanism. The typical sulfite levels carried are at least 50 to 100 mg/L at the coil. While sulfite is the recommended oxygen scavenger, others can be utilized but must be carried at sufficiently high levels to ensure complete oxygen removal from the system before water enters the coils. Since these boilers are prone to failure from oxygen attack, storing idle equipment can be very challenging. It is highly recommended that the plant follow the manufacturer's procedures for lay-up.

Oxygen corrosion typically occurs either during a short-term outage or during lay-up. It can occur in operation, if the system chemistry is insufficient to protect against attack. Oxygen pitting at the upper pancake economizer sections of a vertical coil indicates wet lay-up failure. Pitting in the upper section of a vertical coil also indicates wet lay-up failure. Pitting in the lower sections of either type of system generally indicates dry lay-up failure.

Deposition Coil boilers are very prone to deposition in the form of scale. The temperature profiles generated by the thermocouples over time can indicate if deposition is occurring in the system. In addition to the temperature profiles of the coils, the recirculation pump pressure can be used as an indication of deposition. The pressure rises over time as deposition occurs. Since they are prone to scaling, a polishing softener on the makeup line is common to ensure minimal hardness ingress. Precipitating programs, such as a phosphate program, are typically not recommended for these systems.

Boiler Water Carryover This can be a result of high alkalinity or dissolved solids levels but is often operational in nature. Due to the small steam separating spaces and low steam-to-water ratios (steam reserve capacity) in these boilers, systems with a rapid increase in steam demand can cause carryover. Other areas of investigation for carryover include:

- Operation beyond design capacity
- Water contamination by organics such as hydrocarbons
- Steam separator trap failure
- Erratic operation

Coil Failure from Thermal Stress While the typical overheating failures caused from deposition are common in these boilers, these coils can also fail from other thermal stresses:

- The more the boiler is cycled on and off, the more thermal stress is imparted to the coil. If the mode of operation causes frequent start and stop operation, the boilers are prone to failure.
- Starvation of the coils by partial plugging from chip scale or any other cause quickly results in an overheating failure.
- Feedwater pump failure causes starvation of the coil.

Electric Boilers

The electric or water resistance steam generator has been in existence since 1905. However, the number of these units currently in operation is small. The electric boiler provides some advantages and tangible savings over the more conventional boilers, such as:

- No handling and storage of fuel
- No need for fans, breeching, and chimneys
- No ash handling
- Limited floor space requirements
- Low costs of installation and operation help offset higher electricity costs

Typically, electric boiler designs are limited to less than 600 kWh [2100 lb/h (953 kg/h)] output. However, in some countries where electricity is of particularly low cost, for example, where power is supplied by hydroelectric generation, electric boiler designs of up to 12 000 to 24 000 kWh [42 000–85 000 lb/h (19 000–39 000 kg/h)] or more are commonly used in large process industry applications. The maximum continuous rated (MCR) output is about 220 000 lb/h (100 000 kg/h).

The electric steam generator produces steam rapidly and can be taken off line very quickly. Some units are said to need only five seconds to raise the steam production from 0 to 100%. Roughly, 35 kWh of electricity are required to produce the same heat as one gallon (3.8 L) of No. 6 fuel oil.

Electric boilers are classified as immersion type and electrode type, depending on their method of operation. The immersion-type electric boiler is basically a pressure vessel in which a number of resistance-type heating elements are submerged in water. This type of boiler is generally restricted to the lower capacity applications where steam production is less than 10 000 lb/h (4500 kg/h). The electrode-type boiler, however, uses the conductive and resistive properties of the water itself. A three-phase alternating current passes among three electrodes, with water as the conductor. This is accomplished either by immersing charged electrodes into the water or by spraying water onto the electrodes. Because water has electrical resistance, the current flow generates heat directly in the water. Steam production is a function of the amount of water exposed to the electrodes.

Nuclear Reactor Boilers

Very basically, nuclear energy for steam generation is obtained by the fission (splitting) of the heavy atoms of uranium. The fission process releases tremendous amounts of thermal energy, which can be used to heat water and generate steam.

A nuclear reactor is the equipment used for initiating, maintaining, and controlling a fission chain reaction to gradually release the resultant energy. In a Pressurized Water Reactor (PWR) design, the heat is removed by a closed water system primary loop (Fig. 9.21). The temperature limit of the primary loop is controlled by the rate of fission. This water is sent to a subsequent heat exchanger, where it controls the temperature and pressure of the steam in the boiler (intermediate loop). Special metallurgy limits corrosion and the creation of radioactive isotopes. For more information on nuclear steam generators, refer to Chapter 33 on Power Industry.

Once-Through Boilers

Natural circulation boilers have been designed up to 2850 psig (19.7 MPag). They depend on the circulation of an excess amount of water and the separation of steam from water in some type of drum. This separation is possible because of the difference in density between water and steam. At 2700 psig (18.6 MPag), for example, water weighs 32.9 lb/ft^3 (0.527 g/cm^3) and steam weighs 9.0 lb/ft^3 (0.14 g/cm^3). As the pressure increases beyond 2700 psig (18.6 MPag),

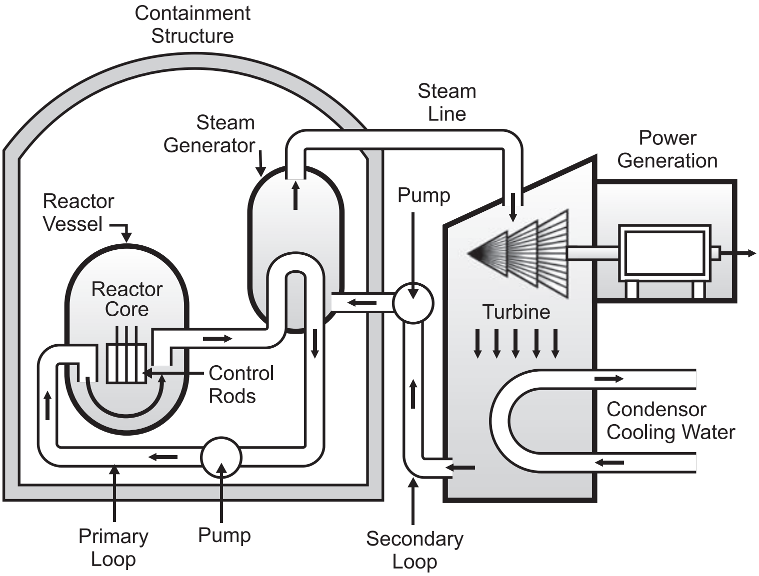


Figure 9.21 Nuclear reactor boiler.

the differences in the steam-water densities become less and less, until at 3200 psig (22.1 MPag), the densities of steam and water are the same.

In a once-through boiler, there is no recirculation of water and no steam drum. As Figs. 9.22 and 9.23 illustrate, water is forced through pipes, where all of it is turned into steam.

Once-through boilers offer some advantages over the more common water-recirculatory units in that once-through boilers are not limited by pressure, there are no drum costs, no recirculatory and downcomer costs, and they have high thermal efficiency.

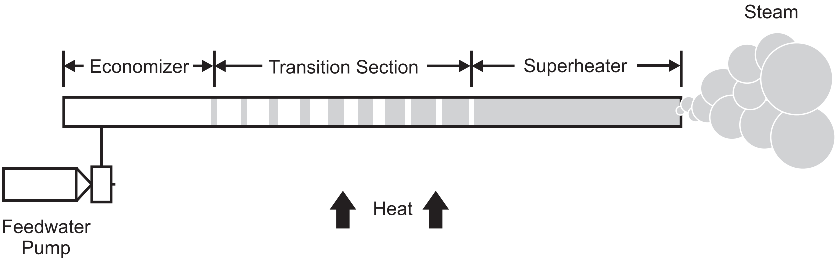


Figure 9.22 Once-through boiler principle.

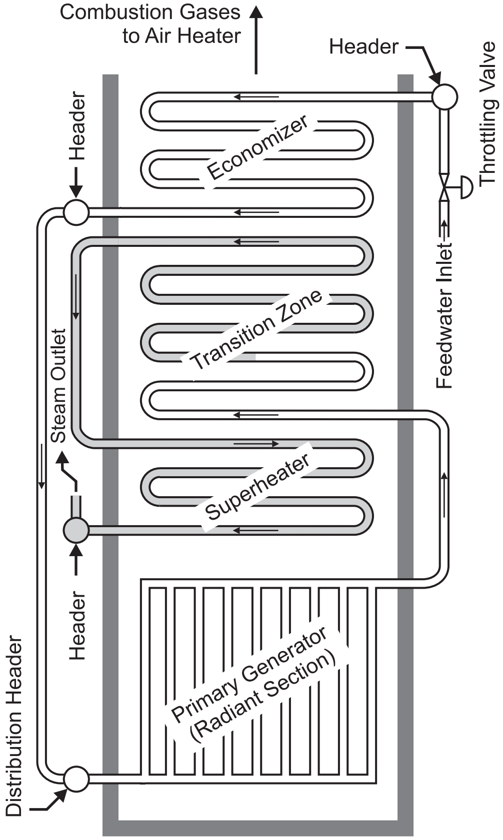


Figure 9.23 Once-through boiler forced flow principle.

Once-through boiler design complexities and feedwater purity requirements limit their usefulness in most industrial applications. Once-through boilers are most commonly found in electric utility plants.

Boiler Ratings

There is no standard means for expressing the capacity or rating of modern steam generation equipment. The capacity of boilers may be stated in terms of area of heating surface, rated boiler horsepower, or maximum steam generating capacity. The boiler horsepower is used only when expressing the capacity of small, simple boilers such as firetube boilers. The capacity of medium and large modern boilers is expressed in maximum mass of steam per hour at a specified feedwater temperature and outlet steam pressure and temperature.

The heating surface of a boiler consists of those areas that are in contact with heated gases on one side and water on the other. The ASME boiler code specifies that the gas side is to be used when calculating heating surfaces. It follows that in determining the heating surface for flue and firetube boilers, the inside diameter of the tubes must be used; for watertube boilers, the outside diameter is used.

The boiler horsepower (rarely used today) is defined as the equivalent evaporation of 34.5 lb/h (15.6 kg/h) of water from and at 212°F (100°C). The energy equivalent is 33 476.73 Btu/h (8436.0 kcal/h, 35 296.2 kJ/h, or 9.8 kW). This expression was derived from an original rating for steam engines stating that for one horsepower of work, approximately 30 lb (13.6 kg) of steam would have to be supplied per hour.

It was further determined that a steel boiler supplying steam for an engine had 10 ft^2 (0.929 m^2) of heating surface for each horsepower. This meant that it had a heat absorption rate of 3347.673 $\text{Btu}/[\text{h}\cdot\text{ft}^2]$ (10.5 kW/m^2) of heating surface. As time passed, more and more boilers were rated in boiler horsepower based on heating surface, that is, one boiler horsepower for every 10 ft^2 (0.929 m^2) of heating surface.

Boilers improved and so did fuel burning equipment and methods. It became apparent that boilers could develop several times the capacity based on former rating methods. Today, boiler horsepower has little correlation to boiler performance. The historical evaporation rate of 34.5 lb steam per hour per 10 ft^2 [16.8 $\text{kg}/(\text{h}\cdot\text{m}^2)$] of boiler heating surface has long since become obsolete. Because of engineering advances, improvements in radiant heat utilization, and better circulation (of both water and gas), the present evaporation rate is greater than 250 lb steam per hour per 10 ft^2 [122 $\text{kg}/(\text{h}\cdot\text{m}^2)$] of heating surface in large utility plant steam generators.

More commonly, the quantity of water evaporated into steam per hour is known as the evaporation rate. The unit evaporation rate is expressed in pounds steam per hour (kg/h), pounds steam per hour per square foot [$\text{kg}/(\text{h}\cdot\text{m}^2)$] of heating surface, or pounds steam per hour per cubic foot [$\text{kg}/(\text{h}\cdot\text{m}^3)$] of furnace volume.

When capacity is expressed in pounds (kilograms) of steam per hour, further information is required, including feedwater temperature; quality (moisture content); steam pressure; steam temperature or degrees of superheat; and specified conditions of fuel, burner, firing method, and draft.

Today, there is a fair degree of standardization for low-pressure heating boilers. Smaller power boilers can be compared based on total heating surface. Some ratings (for packaged units especially) are determined by actual test, accompanied by manufacturer's certification. Large power boilers and utility plant equipment are sold based on performance test after installation.

The purposes of the testing and rating codes adopted by the industry are twofold:

1. To assure the purchaser and specifier that the boiler will actually deliver the output claimed by the manufacturer
2. To provide a basis for comparison between different boilers

Today in the United States, most industrial boilers are built according to the ASME specifications for steam generating units. ASME codes are universally applied; other codes take into consideration specialized designs or pieces of equipment. In Great Britain and Europe, the British Standards Institute (BSI) presents the British view on this subject. Both the ASME and BSI are held in high regard.

The ASME and BSI test codes enable users to obtain accurate information on the adaptability of equipment, best methods of operation, and equipment capacity and efficiency. They provide means for verifying manufacturers' guarantees. The codes also provide checklists before testing, required instrumentation and testing equipment, special precautions, and computation instructions for interpretation of test results.

Boiler Circulation

An adequate flow of water and water-steam mixture is necessary for steam generation and control of tube metal temperatures in all the circuits of the boiler. The force of gravity available to produce flow in natural circulation comes from the difference between the densities [lb/ft^3 (g/cm^3)] of the fluids in the downcomer (downflow) and riser (upflow) tubes (Fig. 9.24).

This flow of water and steam within the boiler is called natural circulation. When heated, water decreases in density and tends to rise to the top of the vessel; conversely, cooler feedwater entering the boiler drum is heavier than the bulk water. Thus, it tends to drop to the bottom of the vessel.

When water is heated to its boiling point, small steam bubbles form on the heated surface. These bubbles cling to the metal due to surface tension until they are large enough to overcome the surface tension or until they are swept away by the circulating water in the tube. This phenomenon is known as nucleate boiling. The steam is much lighter than water and rises rapidly. This movement of the steam through the water creates turbulence and circulation. Figure 9.25 shows the effect of pressure and temperature on steam and water density.

All once-through units and most hot water boilers depend upon positive (forced) recirculation of the water and steam mixture. Nearly all other boilers, however, depend upon natural circulation to ensure that sufficient water is fed to each tube receiving heat to keep its

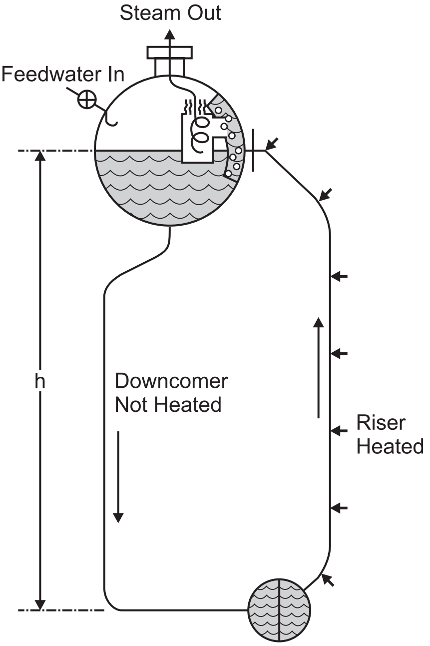


Figure 9.24 Simple natural circulation, including primary steam separator in drum.

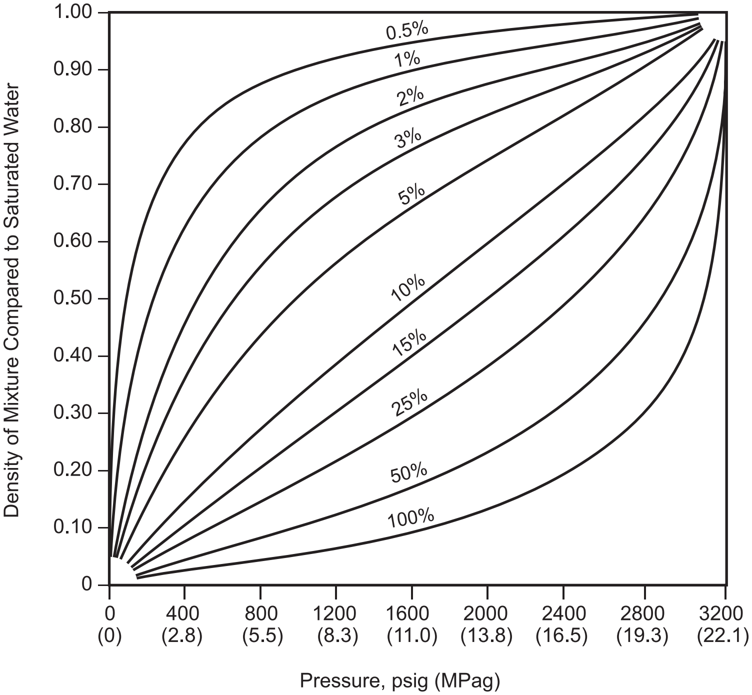


Figure 9.25 Density relationship of steam and water mixture.

surface thoroughly wetted and at the desired operating temperature. Lack of adequate flow will result in tube overheating and failure.

Design Considerations

The prime requisite in designing a natural circulating boiler is to maintain nucleate boiling under all anticipated operating conditions. Equally important is the proper distribution of water to all the tubes, especially in multiple-drum, water-wall boilers.

Water in a large container, for example, a firetube boiler, has a relatively sluggish movement until circulation is established. Staggering of tubes causes greater water turbulence when circulation is initiated. Circulation in watertube boilers, on the other hand, is established quite quickly, beginning as soon as the heat input is sufficient to produce steam bubbles. The steam bubbles create enough density difference within the confines of the tubes to cause water and steam to rise in the riser tubes.

In design, the riser circuits are normally fixed by the general arrangement of the boiler. They form the enclosure of the furnace and provide the surface area required for nucleate boiling, based upon the expected heat absorption (heat transfer rates).

The effect of uneven heating, improper firing, and the burning of different fuels on nucleate boiling must also be considered. The water flow rate velocities in properly designed boilers will ensure that enough water flows over the tubes to pick up the heat required to generate steam, maintain nucleate boiling conditions, and minimize tube overheating and failure. Flow rate velocities vary from 1 to 10 ft/s (0.3–3 m/s), depending upon the type of boiler.

For example, in boilers with inclined tubes, heat flux may be on only half the tube, and the geometry is prone to steam/water stratification (steam blanketing). Therefore, higher mass flows are required to prevent departure from nucleate boiling (DNB). DNB occurs when steam bubbles form faster than they are removed, resulting in an insulating steam blanket. When DNB occurs, the heat transfer through the tube is greatly reduced, overheating occurs, and tubes eventually fail. In boilers that have nearly vertical tubes and total heat flux spread over the entire tube circumference, lower mass flows are adequate.

From an efficiency standpoint, it would be highly desirable to evaporate all the water circulating through the generating tubes in one pass. If this were to happen though, the amount of solids (for a low-purity feedwater system) that would deposit on the high heat transfer surfaces would result in overheating and failure. Total evaporation also presents two other problems:

1. Maintaining a constant water level is almost impossible when load changes occur.
2. Severe foaming occurs due to uncontrolled bubble release.

To overcome these difficulties, boilers are designed to recirculate anywhere from 3 to 30 times more water than is necessary for steam formation. This excess water circulation prevents boiling to dryness and permits easier control of water levels.

The ratio of water fed to the steam generating tubes, and the steam actually generated (mass of water to mass of steam), is called the circulation ratio. Thus, for most recirculating boilers, circulation ratios are normally between 3:1 and 30:1.

As indicated previously, severe tube damage can occur if a boiler does not have proper circulation and flow velocities. The result will be evaporation to dryness, which leads to deposition, tube overheating, and eventual rupture. Evaporation to dryness or steam blanketing may also lead to concentration of chemicals, such as chelates or caustic, causing severe tube corrosion and failure.

Improper heat input and tube design may result in lack of proper circulation velocity. This can be the result of too much heat to the downcomers, causing them to act like riser tubes. Lack of heat to the risers results in insufficient steam generation, causing them to act like downcomers. In either case, the result is inverse circulation or stagnation in the tubes. With these conditions, flow rates are so low that impurities will not be swept along and tend to deposit and accumulate within the tubes, until they are eventually corroded or plugged.

Natural Circulation Systems

As discussed earlier, water circulates naturally because of its change in density with temperature. Thus, in natural circulating systems, boiler circulation increases with increased heat input, until a maximum flow rate is reached. Beyond this maximum point, any further increase in heat input results in a decrease in flow, because the pressure drop in the risers exceeds the head supplied by the downcomers. Properly designed units operate in the rising part of the curve shown in Fig. 9.26, to the left of the maximum peak. Operating in this area of

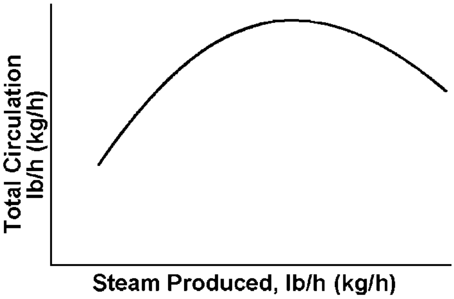


Figure 9.26 Relationship between boiler circulation at a given pressure and steaming rate (scale arbitrary).

the curve permits a natural circulating boiler to be self-compensating under varying load conditions (e.g., increased steam generation under increased load conditions), changes in heat absorption surface cleanliness, and varying fuel and burner conditions.

A natural circulating boiler is the most prevalent type found in today's watertube boilers. Natural circulation is a result of the difference in densities between water and a water-steam mixture. At operating pressures greater than 2500 psig (17.2 MPag) and in some cases where the water-wall tubing is not vertical in orientation, some boiler manufacturers choose to use a forced circulation design rather than natural circulation.

As indicated earlier, too high a heat input can result in restricted circulation and tube starvation. Normally, the first several rows of tubes that are exposed to higher gas temperatures act as risers and the rest as downcomers. With increasing firing rates (higher heat input), the number of tubes acting as risers increases, and the number acting as downcomers decreases correspondingly. When this happens, two problems may occur:

1. There will not be enough downcomers to supply enough water to the risers, and tube starvation results.
2. Some tubes will act as both downcomers and risers, causing reduced flow or stagnation (dead spot).

Boilers with water-cooled furnace walls may experience problems if there is not proper circulation. These tubes absorb radiant heat at such a rapid rate that steam forms a large part of the tube contents near the top of the wall. Boiler manufacturers take extreme caution to ensure that water-wall downcomers are large enough to supply sufficient water to the wall riser tubes, and are properly insulated to protect against becoming risers as well. Lack of proper circulation in the water-wall tubes results in rapid and massive tube failures.

Positive (Forced) Circulating Systems

Essentially, positive circulation uses recirculating pumps to force the water to circulate through the boiler, for example, as cooling water must be circulated. Some manufacturers choose to use the forced circulation design for units operating at 2500 psig (17.2 MPag) or greater because of the low density ratio between steam and water. For example, at 500 psig (3.4 MPag), the density ratio between water and steam is 50:1; however, at 2500 psig (17.2 MPag), this ratio is only 5:1.

Because positive circulating boilers do not require natural circulation, they can be designed to make the most efficient use of available space. Tubes may be arranged horizontally and of any number of different sizes and passes, because water flow can be proportioned at the inlet when utilizing positive circulation to flow through all tubes at desired rates.

Once-Through Circulation

In once-through units, feedwater is forced through the circuits with all of the water turning to steam. In other words, unlike recirculating systems that require circulation ratios of 3:1 to 30:1, a once-through unit has a circulation ratio of 1:1. Once-through units can be likened to a long pipe, where water is put into one end and comes out as steam at the other end. These units may operate either at subcritical or supercritical pressures [3200.2 psia (22.1 MPaa) is defined as the critical pressure of water]. They have limited application in industry, but are widely accepted in electric utilities.

For a further explanation of the design and operation of once-through units, refer to once-through boilers earlier in this chapter.

CHAPTER 10

Oxygen Removal

After pretreatment, corrosive gases such as carbon dioxide (CO_2) and oxygen (O_2) must still be removed from the feedwater system. Mechanical deaeration can remove these gases, especially oxygen, reducing them to a level that is either acceptable to the boiler system or suitable for further application of scavenging chemicals. Because oxygen is highly corrosive to metal, it must be reduced to the lowest possible concentration. Mechanical deaeration can reduce the concentration to less than 7 µg/L, depending on the equipment design and operation.

Oxygen is a highly active element. Even in small amounts, it can cause serious corrosion in feedwater lines, economizers, boiler internals, steam-operated equipment, and condensate return piping. Corrosion increases with increasing oxygen content. The corrosion rate of oxygen dissolved in water doubles for each 18°F (10°C) increase in temperature. In addition, portions of a system that are exposed to high flow rates or turbulent flow conditions are more susceptible to oxygen attack.

When oxygen and carbon dioxide are present together, the resulting corrosion rate may be 10 to 40% greater than the sum of the corrosion rates of the two gases acting separately. The combination of oxygen and ammonia is very corrosive to copper alloys.

Corrosion Mechanisms

Corrosion is an electrochemical process. Iron dissolves at the anodes, releasing electrons that are subsequently consumed by oxygen at the cathode (see Fig. 10.1). At a pH of approximately 7, the half-cell reactions are as follows:

Anode: $$Fe^0 \rightarrow Fe^{+2} + 2e^- \tag{10.1}$$

Cathode: $$2e^- + H_2O + \tfrac{1}{2}O_2 \rightarrow 2OH^- \tag{10.2}$$

Penetration at the anodic area depends on the relative size of the cathodic and anodic areas. A small anodic area and a large cathodic area, for example, results in a concentrated dissolution of the iron at

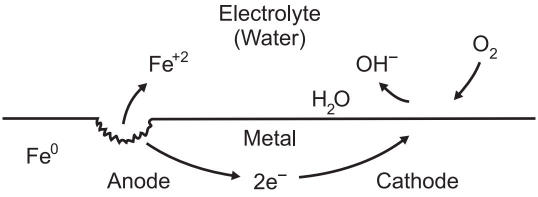


Figure 10.1 Corrosion cell mechanism.

the anode to provide electrons for the larger cathode. As a result, a deep pit forms at the anode. Conditions that favor the formation of relatively small anodic areas are oxygen concentration differentials under areas of sludge accumulation, localized stress, and breaks in the passive magnetite layer on the steel surface.

Figure 10.2 illustrates oxygen corrosion located under a typical tubercle. Figure 10.3 illustrates the pitting of a similar metal surface after all sludge and iron oxide buildups have been removed.

Because of oxygen's corrosive tendencies, feedwater is usually deaerated to remove as much of the gas as possible. Commonly, this is accomplished mechanically in a pressure deaerator. However, other devices and methods of removal are available and are discussed in the sections that follow. These include:

- Vacuum deaerators
- Feedwater heaters

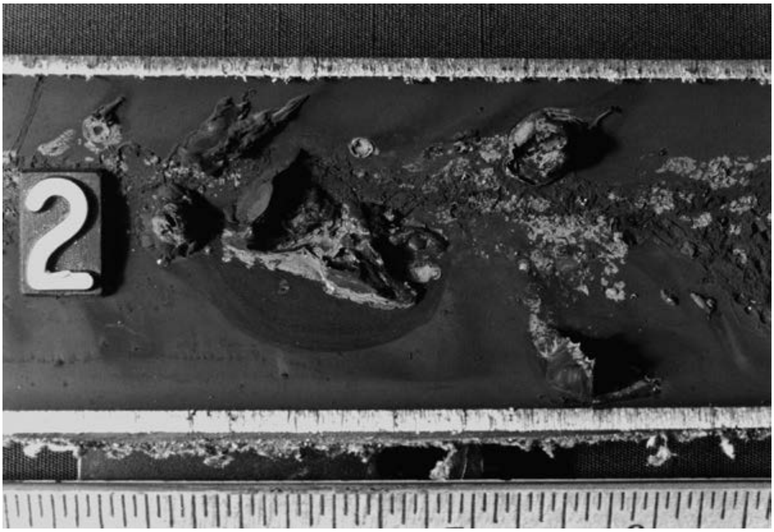


Figure 10.2 Oxygen corrosion tubercle.

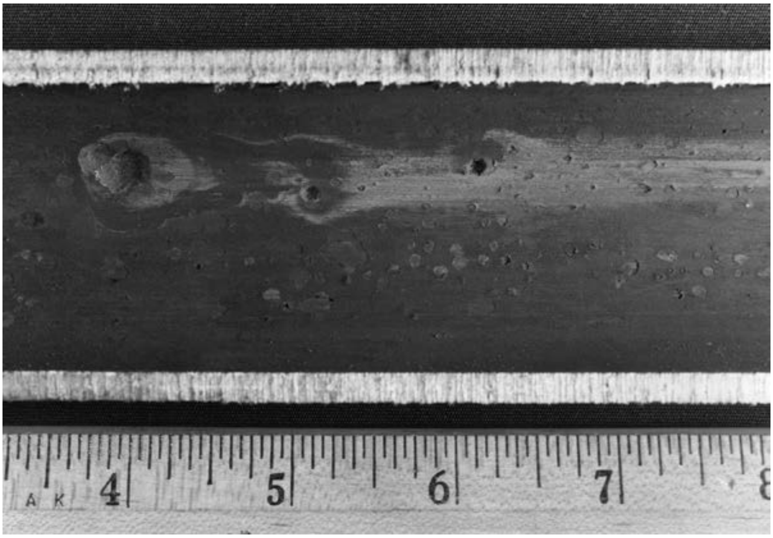


Figure 10.3 Pitting caused by oxygen corrosion.

- Deaerating condensers
- Gas transfer membrane systems
- Carbon beds with scavenger activation (catalysis)
- Ion exchange resin catalysis

Because such units or systems (including pressure deaerators) rely on equilibrium conditions, they cannot completely remove all oxygen present; so supplemental chemicals are needed to reduce the remaining residual oxygen further.

Mechanical Deaeration

Mechanical deaeration is the physical removal of dissolved gases from water. The primary goal is to remove oxygen from the boiler feedwater, but carbon dioxide and ammonia (NH_3) can also be reduced by deaeration. Effective removal of ammonia by mechanical deaeration requires a special design, as removal in standard deaerators is inefficient.

Mechanical deaeration is influenced by the following physical-chemical considerations.

Ionization

The degree to which gases can be deaerated depends on the ionization state of the gases involved. Oxygen does not ionize; therefore, it is easily removed. Carbon dioxide and ammonia do ionize, as shown in the following equations:

$$CO_2 + H_2O \rightarrow H_2CO_3 \rightarrow H^+ + HCO_3^- \qquad (10.3)$$

$$NH_3 + H_2O \rightarrow NH_4OH \rightarrow NH_4^+ + OH^- \qquad (10.4)$$

Only that portion of these gases that remains in nonionized molecular form (CO_2 and NH_3) can be removed by mechanical deaeration. However, since ionization is an equilibrium state, adding mineral acids to the carbonic acid and alkali to the ammonium will shift these equilibria back toward the formation of CO_2 and NH_3. Figures 10.4 and 10.5 show the effect of pH on the portions of these two gases that are available for mechanical removal.

Thus, a mechanical decarbonator inserted after a hydrogen cycle cation exchanger, can remove carbonate alkalinity by stripping CO_2 from the water. This operation is quite efficient and removes CO_2 down to 5 to 10 mg/L in an atmospheric, blower-type unit, and down to virtually zero in a vacuum unit. If the decarbonator were placed into the flow before the hydrogen cycle cation exchanger acidified the water, CO_2 removal would be very poor.

Relative Partial Pressure

Water will dissolve a free (nonionized) gas only to the point at which equilibrium is reached between the partial pressure of the gas in the water and the partial pressure of the gas in the atmosphere with which it is in contact. This is Henry's law.

Air contains approximately 20% oxygen (O_2) and 79% nitrogen (N_2). The partial pressure exerted by oxygen in air is 1/5 atmosphere (20/100). Water surrounded by air, therefore, can dissolve oxygen

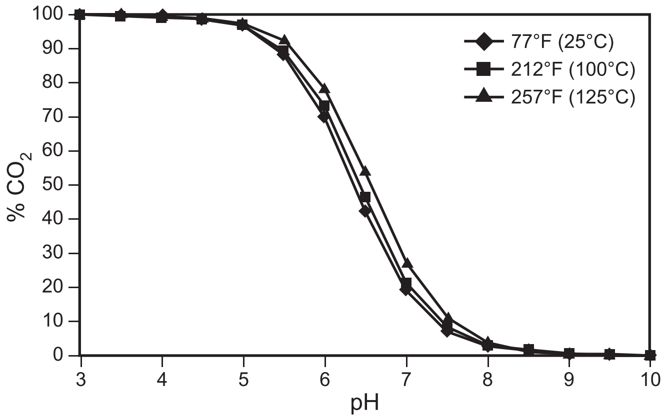


FIGURE 10.4 Carbon dioxide concentration versus pH.

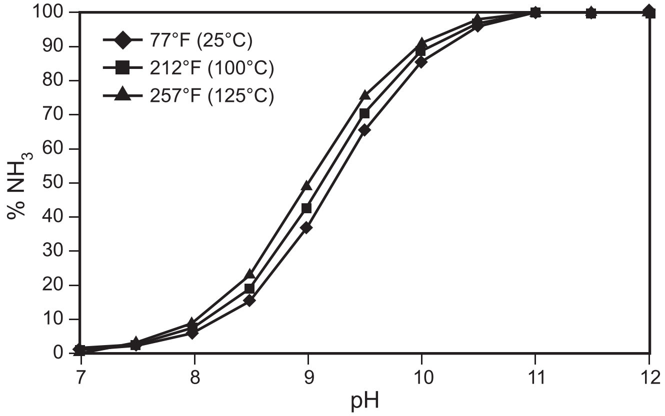


Figure 10.5 Ammonia concentration versus pH.

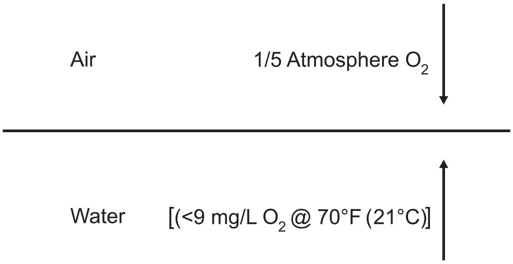


Figure 10.6 Equilibrium between O_2 in air and O_2 in water.

up to the point at which oxygen in the water exerts a partial pressure of 1/5 atmosphere (see Fig. 10.6).

At 77°F (25°C) and atmospheric pressure, this correlates to an approximate content of 8.4 mg/L oxygen in water. In traditional mechanical deaeration, the equilibrium between oxygen in the water and the atmosphere contacting it is deliberately upset. This is accomplished by blanketing the water with an atmosphere of steam that contains little oxygen (see Fig. 10.7).

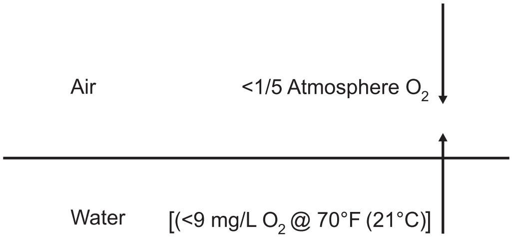


Figure 10.7 Equilibrium shift with steam.

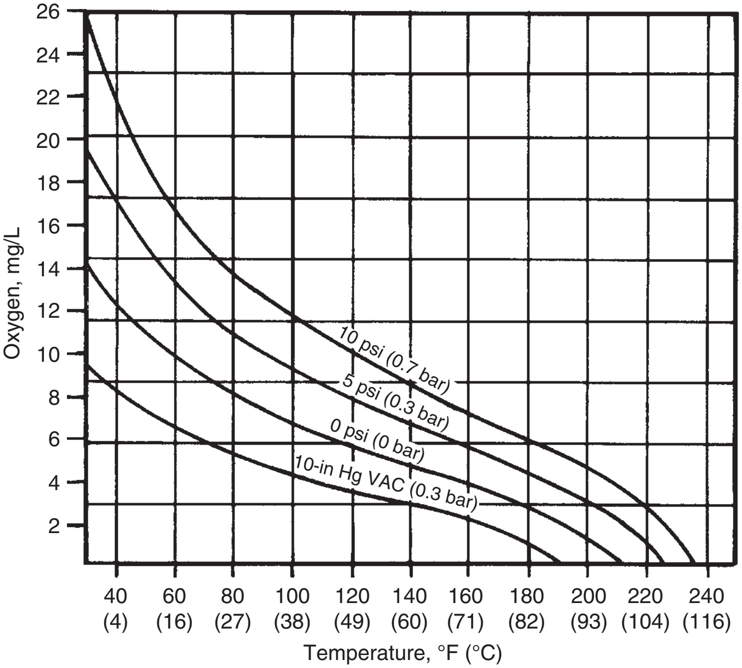


Figure 10.8 Solubility of oxygen in pure water versus temperature.

Temperature

As the temperature of water is raised to its boiling point (saturation temperature for a specific pressure), all free (nonionized) gases theoretically become insoluble. Figure 10.8 graphically illustrates the solubility of oxygen as a function of temperature. In practice, total removal of gases does not occur. Henry's law relates the steam oxygen content to the liquid water oxygen content. As a result, neither of these contents can reach zero, and a small amount of gas remains dissolved in the water phase.

Agitation

A more complete removal of entrapped gases can be obtained by breaking the water stream into small droplets or thin films and then preventing these droplets from agglomerating. Smaller droplets can be heated more efficiently, and the vapor/liquid interface will be repeatedly broken, reducing the tendency of the gases to remain dissolved in the cooler liquid phase. With a smaller droplet, the entrapped gases have a shorter distance through which to diffuse before release from the water. Steam can more effectively scrub the smaller droplets. Finally, by continuously breaking and reforming

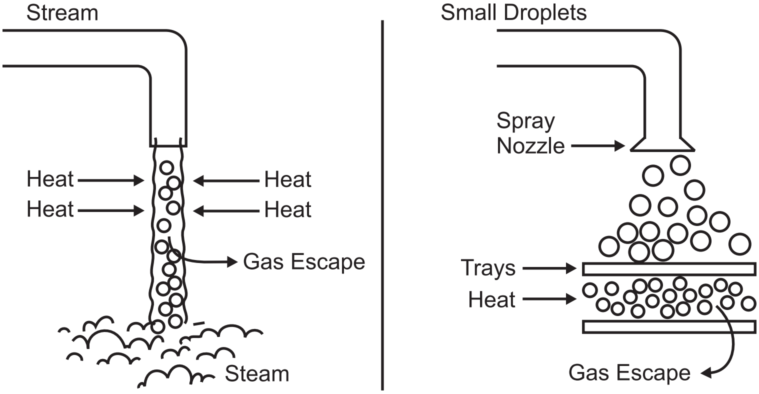


FIGURE 10.9 Gas removal from water droplets.

the droplets of water, entrapped gases have a greater tendency to escape from the water (see Fig. 10.9).

Gas Removal

The gases released from the water must be physically removed, or they will redissolve. Removal is accomplished by maintaining a flow of fresh steam over the droplets, directing the oxygen contaminated steam away from the deaerated water, and finally by removing the liberated gases from the system. In mechanical deaeration, removal is accomplished by continuously venting the gases to atmosphere.

The following sections describe how these principles are incorporated in the designs of the various types of mechanical deaerators.

Pressure Deaerators

Deaerating equipment is designed to heat water to the temperature of saturated steam at the pressure maintained within the deaerator and to reduce oxygen in the feedwater to about 0.007 to 0.04 mg/L (7–40 μg/L). If the unit is guaranteed to reduce the oxygen to 7 μg/L or less, it is commonly designated as a deaerator. If the equipment is guaranteed to reduce oxygen to only 40 μg/L, it is commonly referred to as a deaerating heater.

Designs vary from manufacturer to manufacturer, so units encountered in plants may deviate from the examples illustrated or described here. It is wise to compare the actual internal and external configurations and operating conditions with the original drawings and specifications. Poorly planned retrofits, construction modifications, or changes in system conditions such as for energy recovery are often the cause of poor deaerator performance.

Deaerating units may be spray, tray, or atomization type, but all three types have two distinct sections. These are the primary preheating section and the secondary deaeration section. The preheating section in all types of modern pressure deaerators is of similar design, construction, and function regardless of the type of secondary deaeration element.

Primary Preheating Section

The function of the primary preheating section is to raise the temperature of the water entering the deaerator to within 1 to 2°F (0.6–1.1°C) of the saturation temperature of the steam being used. In addition, this section functions as the vent condenser to condense the steam, liberate the noncondensable gases, and release the gases to atmosphere. Continuous condensation of the steam at this point causes fresh steam to flow continuously through the secondary deaeration element in order to maintain the operating pressure. This action ensures the required atmosphere of oxygen-free steam is maintained to sustain good deaeration.

In older units, the vent condenser consisted of a tubular heat exchanger usually mounted in a cast iron housing located externally on the top of the unit. The liquid entering the deaerator flowed through the tubes inside the steam atmosphere of the cast iron shell. After being heated in the tubes, the liquid was usually sprayed into the steam atmosphere in the deaerator through one or more perforated spray pipes.

In newer deaerators, the heat exchanger and spray pipes have been replaced by a preheater section with a number of stainless steel, spring-loaded spray nozzles. The nozzles create very thin curtains of water that reach saturation temperature very rapidly and release over 90 to 95% of the dissolved oxygen and other noncondensable gases.

The preheater section also serves as an internal, direct-contact vent condenser, where noncondensable gases are separated and concentrated before being discharged to atmosphere. The mixture of steam and noncondensable gases (including oxygen) present in the preheater section, is in intimate contact with the incoming cold water, so that most of the steam is condensed in the heating of the water. Only a small amount of steam along with the oxygen and other noncondensable gases is discharged through the vent pipe to atmosphere. Condensation of the steam in the preheater is the only mechanism that maintains the required steam flow through the secondary section, since the amount of steam passing through the vent valve is very small.

In very large, horizontal deaerators installed in high-pressure utility stations, the preheater may still consist of perforated spray pipes. In such cases, the operating load tends to be almost constant, and makeup is a small percentage of the feedwater. Accordingly, the fixed orifices in the spray pipes usually can maintain the desired pressure drop, thin water curtains, and degree of preheating required to maintain guaranteed performance.

Regardless of the preheater or deaerator type, the operation of the preheater is crucial to successful deaeration. Unless the preheater reduces the oxygen level to a few hundred μg/L (<5–10% of the original concentration), the secondary deaeration section will be unable to reduce the final effluent oxygen residual to the guaranteed level. As long as the springs are intact and maintain the desired pressure drop, the preheater will function as required over much of the unit operating capacity range.

Basic Principles of Mechanical Deaeration Using Pressure Deaerators

Effective mechanical deaerators must accomplish the following:

- Heat the water to the saturation temperature corresponding to the steam pressure within the deaerator.
- Break the water stream into small droplets or thin films that allow rapid diffusion of gases to a water surface, where they can be liberated into the vapor phase.
- Vigorously boil and scrub the heated water with fresh, oxygen-free steam that removes any remaining traces of oxygen and other noncondensable gases.
- Maintain the partial pressures of oxygen and carbon dioxide as low as possible at the liquid and vapor interface, especially where deaerated water separates from steam.
- Continuously discharge the noncondensable gases from the space within the deaerator dome through proper venting.

Spray Deaerator

Figure 10.10 illustrates a typical spray-type deaerator. It may be more accurately described as a fixed orifice scrubber or reboiler. As previously discussed, feedwater enters the primary preheater section through spring-loaded spray valves. Steam supplied to the primary preheater section comes from the secondary stage deaerator.

Feedwater leaving the primary preheater section contains only traces of oxygen and other noncondensable gases. The water enters the second-stage scrubber section, flowing through internal piping or channels. The hot water mixes with live, fresh steam, which has entered the scrubber section through the steam inlet. It is important

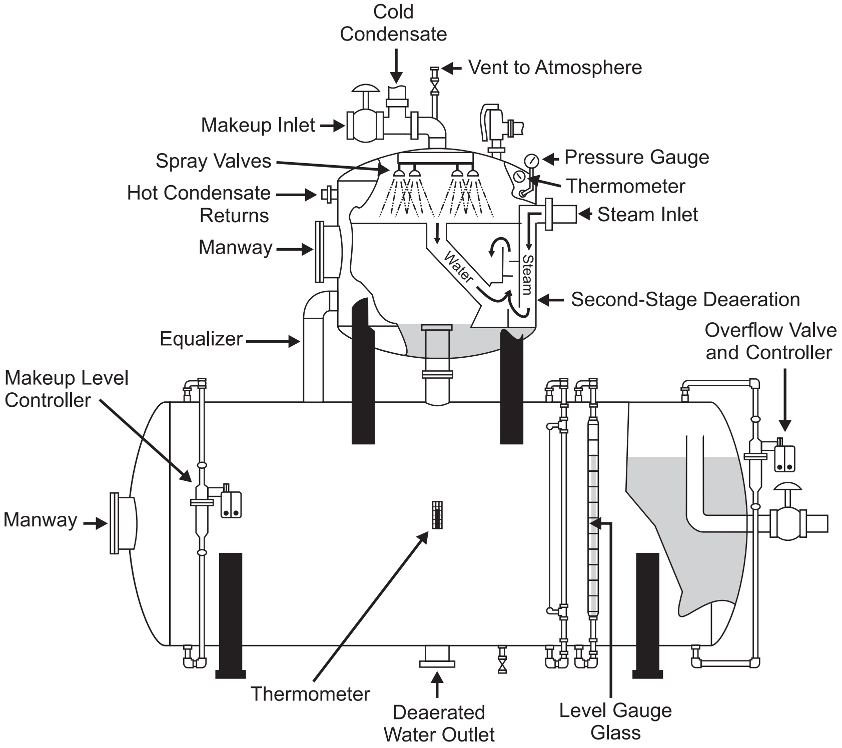


Figure 10.10 Spray deaerator.

to realize that the volumetric ratio of the resulting mixture will be approximately 99.6% steam/0.4% water as opposed to a ratio of approximately 1% steam/99% water based on mass. For example, saturated steam at 20 psia (138 kPaa) has a specific volume of 20.079 ft^3/lb (1.253 m^3/kg), while the saturated liquid has a volume 0.017 ft^3/lb (0.001 m^3/kg). This vast difference in volume has an extremely vital impact on the performance of a spray deaerator.

Both steam and water enter the bottom of the scrubber pot or chamber, where the two form an intimate mixture that is heated to full saturation temperature. As the mixture flows upwards, it may first pass through a distribution orifice or port that imposes a negligible pressure drop. At the outlet or throat of the scrubber, the mixture must pass through a final fixed area orifice, which imparts a significant pressure drop on the mixture. The drop in pressure creates a superheated mixture that immediately boils as it leaves the scrubber. This action scrubs the final remnants of oxygen from the mixture. The deaerated water falls to the storage area, while the steam and noncondensables are drawn into the preheater section.

The scrubber is a fixed orifice device that is designed and sized relative to a certain steam volume and velocity. Any change in operating conditions that creates a substantial change in steam volume or velocity will have a negative impact on deaerator performance. For example, a sharp increase in influent temperature would reduce steam demand, decrease scrubber steam velocity, and reduce stripping action. The addition of heat recovery equipment upstream of the deaerator could be the cause of such a condition. On the other hand, a sharp decrease in influent temperature could increase steam demand so dramatically as to cause a sudden and inordinately large increase in steam velocity. This could prevent good stripping action, promote entrainment of water in the vent vapor, and even damage the deaerator internals. Cold system start-ups at heavy flow rates or sudden surges of cold makeup water are typical causes of this condition.

Spray deaerators work well in base-load applications, where variations in influent flows are minor and predictable. They work quite well when operated at or near average design flow conditions. However, with wide load swings and operating conditions that vary considerably, they fail to produce the low effluent oxygen desired.

Tray Deaerator

Figure 10.11 illustrates a tray-type deaerator. As previously discussed, feedwater enters the primary preheater section through spring-loaded spray valves. Steam supplied to the primary preheater section comes from the secondary stage deaerator.

The preheated water, which has little oxygen or noncondensables remaining (<5–10% of the original concentrations), is then directed into the secondary deaerating section. This is typically an enclosed stack of distributing pans or trays of stainless steel construction. In some designs, the lower trays may be replaced by stainless steel random ring packing.

The preheated water spills uniformly over the tray stacks or packing and cascades downward forming thin, uniform films. These thin films or curtains of water allow the oxygen to diffuse rapidly to the surface, where the equilibrium allows it to escape into the vapor phase or steam.

Steam flow in the tray section may take one of three configurations: co-flow, cross-flow, or counter-flow. In a co-flow unit, the steam is introduced at the top of the tray bank and flows down through the trays with the water. In a cross-flow unit, the steam passes from left to right as the water descends through it. In a counter-flow unit, the steam is introduced at the bottom of the tray stack and passes up through the descending water. This is probably the best of the three designs, since the cleanest steam mixes with the cleanest water at the bottom of the tray stack. Because of the condensing effect in the

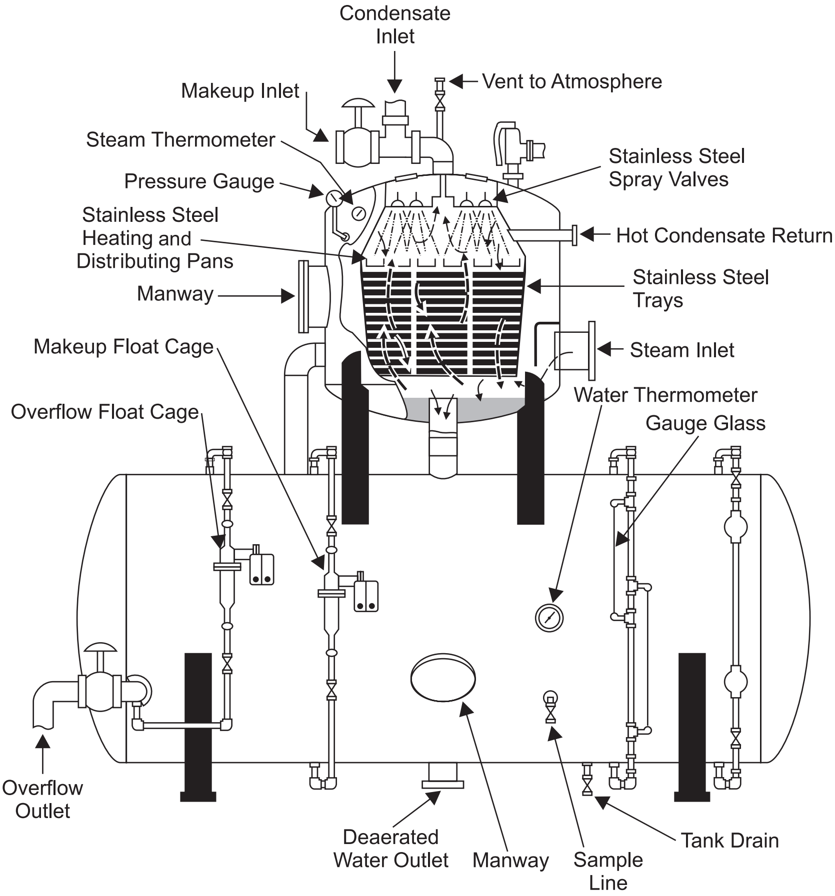


Figure 10.11 Tray deaerator.

internal vent condenser/preheater section, and regardless of configuration or design, steam must flow from the steam inlet through the secondary tray section to the primary preheater section.

In the design using random packing, the steam is admitted at the bottom flowing upward through the packing in one pass and counter-current to the water flow. Again, steam flow is assured by the condensing effect in the preheater section. When the steam condenses, it falls back into the distributing pans with the incoming water that has been preheated. The noncondensable gases are released to atmosphere through the vent.

The tray deaerator is ideally suited for wide load swings or operation at partial loads, because of the capability of the tray stack to distribute and detain the falling water resulting in longer, more intimate steam-water contact. Thus, the tray deaerator is more tolerant of variations in steam flow and velocity. Steam flow through the tray section, however, must be sufficient to maintain water contact with oxygen-free steam and to maintain the desired equilibrium conditions necessary for full deaeration. Steam flow can only be maintained by condensation of steam in the preheater section as the feedwater is heated to saturation temperature.

Atomizing Deaerator

Figure 10.12 illustrates a typical design for a variable orifice atomizing deaerator. Note that this figure shows an external vent condenser.

As with the other types of deaerators, this type of unit is equipped with a primary preheater. The preheated, partially deaerated water then falls on the collecting cone, which directs the water to the atomizer.

Steam enters through the side of the deaerator and is conducted to the atomizing valve, where it is discharged as a constant high-velocity steam jet. The energy of the steam jet breaks up the water, producing a mist or fog of finely divided particles to assure maximum surface exposure to the scrubbing steam. Any remaining gas is removed and carried to the first stage by the steam, while the deaerated water falls to the storage section.

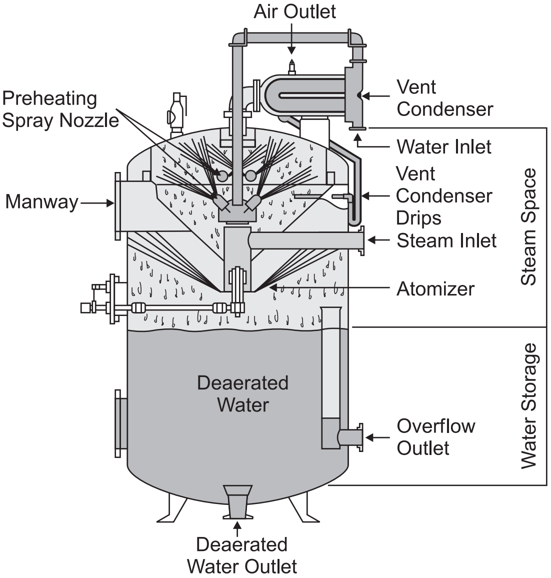


Figure 10.12 Atomizing deaerator.

The atomizing valve is a variable orifice that is controlled either by integral, internal springs or weights or by an external weight-loaded arm. It is self-compensating and maintains a constant pressure differential on the steam supply, regardless of the load at which the deaerator is operated or the temperature at which the water is received. The steam jet is created by imposing a pressure drop through the orifice. As long as the internal valve is operable, the pressure drop is relatively constant. However, if the internal valve or lever linkage seizes or becomes inoperable, the unit becomes a fixed orifice device, and the resulting steam jet velocity is unpredictably variable.

Operating Considerations for Pressure Deaerators

All liquids having a temperature lower than the saturation temperature of the operating steam, should enter the deaerator through the spray nozzles or spray pipe. All liquids having a temperature higher than the saturation temperature of the operating steam, should enter the unit as follows:

- For spray-type deaerators, high-temperature liquids should enter directly into the scrubber pot upstream of the scrubber orifice.
- For tray-type deaerators, high-temperature liquids should enter such that the resulting flash steam travels through the trays using the same path as fresh steam.
- For atomizing-type deaerators, high-temperature liquids should enter directly into the preheater section above the atomizing valve, where the flash steam will be used in preheating.
- Introducing high-temperature liquids in other locations will adversely affect deaerator performance.

Changes in operating steam pressure will affect deaeration efficiency. Therefore, the sensing connection of the operating steam pressure control valve should be connected directly to the steam dome within the steam space of the preheater and should not be connected to the steam supply header outside the deaerator.

The differential between the mean temperature of the total liquid mixture entering the deaerator and the saturation temperature for the operating steam pressure should be more than 30°F (17°C), to assure adequate flow of scrubbing steam in the secondary deaeration section. A tray-type deaerator might perform satisfactorily down to a 10 to 20°F (6–11°C) temperature differential. Increased plant heat recovery initiatives may have a great impact on deaeration efficiency and chemical scavenger dosage by increasing the mean inlet liquid temperature.

If a tray or atomizing deaerator is operating below 25% of its design capacity, oxygen removal efficiency will be lower and scavenger chemical dosage will be higher than expected. A measurement greater than 15 μg/L O_2 is indicative of a poorly operating deaerator.

The temperature of the stored deaerated water should be within 1 to 4°F (0.6–2.2°C) of the saturation temperature for the operating steam pressure. Failure to achieve this temperature differential results in high effluent oxygen concentration and indicates mechanical issues within the unit.

Deaerating Heater

A deaerating heater is similar in most respects to tray, spray, and atomizing deaerators and typically cannot be discerned by external inspection. The major difference is the secondary deaeration section does not provide the same amount of steam/water contact or agitation as a full deaerator. In addition, the trays will probably be made of cast iron construction. Deaerating heaters will usually be guaranteed for an effluent oxygen of 40 μg/L, which is significantly higher than the effluent oxygen concentration from a full deaerator. Few new units are being built today, although deaerating heaters can still be found operating in older, low-pressure steam plants.

Proper Venting of Pressure Deaerators

One of the most common causes of poor deaerator performance is insufficient venting due to valve closure or restriction of vented steam, most typically for energy conservation purposes. The deaerator vent is one of the few points in the system where dissolved gases may be removed. Deaerator venting is analogous to the continuous blowdown of dissolved solids from a boiler. Dissolved solids cannot be discharged from a boiler drum without loss of some carrier water. Similarly, dissolved gases cannot be discharged from the deaerator without loss of some carrier steam. Noncondensable gases not vented from the deaerator will concentrate in the vapor phase, increasing their partial pressure. This in turn, increases their concentration in the liquid phase or deaerator effluent. Insufficient discharge of dissolved gases may cause major damage to power train components that can result in plant shutdown or equipment replacement.

Energy conservation measures frequently result in the installation of heat exchangers, cooling jackets, or other devices, to reclaim the heat content of the vent steam containing the noncondensables. Many of these devices cause a backpressure on the vent line and thus restrict flow. The result is higher noncondensable gases in the deaerator effluent.

In some cases, vent steam flow is reduced because of a choked or plugged orifice. Steam may condense in vertical or non-vertical vent pipes. This condensate flows back down the pipe walls, choking the vent orifice when steam flow is not sufficient. To minimize this type of problem, vent piping should be installed with no sharp bends or traps that could pool condensation and obstruct the flow of gases. Cooling water leaks in an external vent condenser, can cause excess water accumulation in the shell. If the drainpipe cannot discharge the excess liquid or is plugged, gas flow to the vent will be restricted.

Proper venting of a deaerator should result in a strong visible plume. There should be an invisible or clear area of approximately 6 to 18 inches (150–460 mm) between the end of the vent pipe and the visible portion of the plume. Irregular spitting of water with the vent discharge can indicate condensation, internal leaks, or water entrainment from broken or damaged spray nozzles. This condition, whatever the cause, can choke the vent gas flow.

Typically, the maximum quantity of steam required for venting a properly operating deaerator is less than 0.2% of the feedwater flow. This value varies relative to the percentage of fresh makeup used, but is less than 0.2% for tray or spray deaerators operating with 100% makeup. Some deaerator manufacturers might conservatively recommend 0.5% to assure sufficient venting.

Mixing Condensate and Makeup

One role of the deaerator is as a receiver for a variety of water, steam, and hot condensate streams that need to be recovered. It is important that these be introduced into the deaerator in such a manner as to avoid extreme temperature interfaces and to permit smooth operation.

A common practice is the separate introduction of the return condensate and cold makeup streams into the deaerator water box or preheater sprays. A large temperature differential between the two streams [more than 80°F (44°C)] can result in thermal stresses and water hammer that can damage deaerator components.

Separate condensate and makeup connections can significantly affect performance in a tray-type deaerator. The amount of mixing that actually occurs in the water box is minimal, and the water spraying out of the water box tends to divide the preheater and tray sections into hot and cold zones. This creates an imbalance of steam flow through the tray stack with the steam gravitating to the cold side. The performance impact of this condition will depend on the temperature difference between zones.

A condensate receiver operating at atmospheric pressure upstream of the deaerator can help provide system stability. Its function is to receive and mix the makeup and condensate such that their flows and temperatures will be smoothed prior to introduction into the deaerator. This alleviates the problem of thermal stresses, water hammer, or performance degradation caused by separate makeup and condensate connections at the deaerator.

The condensate receiver should ideally be located downstream of the heat recovery equipment so that it can vent any free air or noncondensables released by the temperature increase. It should be constructed of stainless steel or lined properly to accommodate the more aggressive water resulting from the mix of cold, oxygen-laden makeup and hot condensate. Water inlets should be designed at opposite sides near the top, and the suction outlet should be at the bottom. The vessel needs to be sized for low-flow velocity and good mixing so that free air release will occur. A check valve should also be included in the line from receiver to deaerator to prevent backflow during shutdown.

If a condensate receiver is absent and cannot be installed, the use of separate condensate and makeup connections should still be avoided. This can be accomplished by joining the two flows at a stainless steel tee connection prior to their entry into the deaerator. The connection should be located a minimum of ten inlet pipe diameters upstream of the deaerator to assure good mixing. A stainless steel tee is required because the blend of cold makeup water and hot steam condensate is extremely corrosive, and mild steel piping will corrode and fail prematurely.

Pressure Deaerator Problems

Poor deaerator performance is usually the result of either a mechanical malfunction or improper operation, especially flow control. Improperly operating deaerators are usually the result of one or more of the following factors:

- Inadequate venting
- Inadequate quantities of steam or steam pressure fluctuation
- Wide fluctuations in feedwater flow
- Feedwater flow rates outside design specifications (above or below)
- Insufficient differential between the influent feedwater temperature and the saturation temperature for the operating steam pressure
- Malfunctioning (plugged or broken) or missing spray nozzles, trays, or atomizing valves

These problems will usually be indicated by a broad temperature differential [>4°F (2.2°C)] between the dome (deaerating section) and the storage section of the unit and by excessive dissolved oxygen in the effluent (more than 15 μg/L for deaerators or more than 60 μg/L for deaerating heaters).

Vacuum Deaerators

Vacuum deaerators remove oxygen and other gases from water at temperatures below the atmospheric boiling point. In some instances, it is undesirable to heat water to accomplish full deaeration, or steam is unavailable to operate pressure deaerators. Examples are process water applications in synthetic fiber plants, desalination, beer and soft drink bottling plants, downhole injection water for water-flood enhanced oil production, water distribution systems, and other processes requiring gas removal without an increase in product temperature. The process is sometimes referred to as cold water deaeration.

The principles employed in vacuum deaeration are the same as those previously described for pressure deaeration, except that the water is not heated to steam temperature. Rather, the water is brought to the boiling point without being heated by lowering its pressure with vacuum equipment. The amount of vacuum necessary is dictated by the vapor pressure of the water at its ambient temperature. For instance, water at 41°F (5°C) will boil in a vacuum of 29.7 inches mercury (754 mm Hg), which corresponds to a pressure of 0.13 psia (0.9 kPaa). At 68°F (20°C), the vacuum required is 29.2 inches mercury (742 mm Hg) or 0.34 psia (2.3 kPaa).

The water vapor produced under vacuum is mixed with oxygen and other noncondensable gases. Low partial pressures of these gases are maintained at the steam/water interface, because of dilution by the water vapor and continuous removal by the vacuum system. Agitation and surface exposure is partially accomplished by spraying the water through spray nozzles or perforated spray pipes. The thin curtains and small droplets of water facilitate diffusion of all gases into the vapor phase in a manner similar to the preheater section in a pressure deaerator. Initial spraying removes the bulk of the noncondensable gases present in the inlet water. Additional agitation is provided by allowing the water to trickle down over trays or suitable random synthetic packing. The vapor, contaminated with the removed gases, is extracted from the unit by the vacuum equipment, condensed where possible, and discharged to waste.

The deaerated water is collected in the integral storage section and pumped to the point of use. Because of the vacuum held in the unit, the deaerator must be elevated at a height suitable for the transfer pump net positive suction head (NPSH) requirement. In addition, the vessel must be designed to withstand full internal vacuum conditions without any penetration of air, that is, it must be perfectly airtight.

The temperature of the water to be deaerated has a marked effect on the physical design of the unit as well as the required capacity of the vacuum equipment. Vacuum is exerted on the vessel using vacuum pumps or, if motive steam is available, multistage steam jet ejectors with inter-condensers. In applications where motive steam for ejectors is unavailable, vacuum pumps must be used, and capital costs can be very high.

Deaerating Condensers

Under favorable conditions and with the proper design, the steam condenser (Fig. 10.13) is probably as good as any available pressure deaerator. Condenser deaeration is performed under vacuum, and many of the principals are the same as previously discussed for vacuum deaeration. A significant difference, however, is that air inleakage is always present in steam condensers.

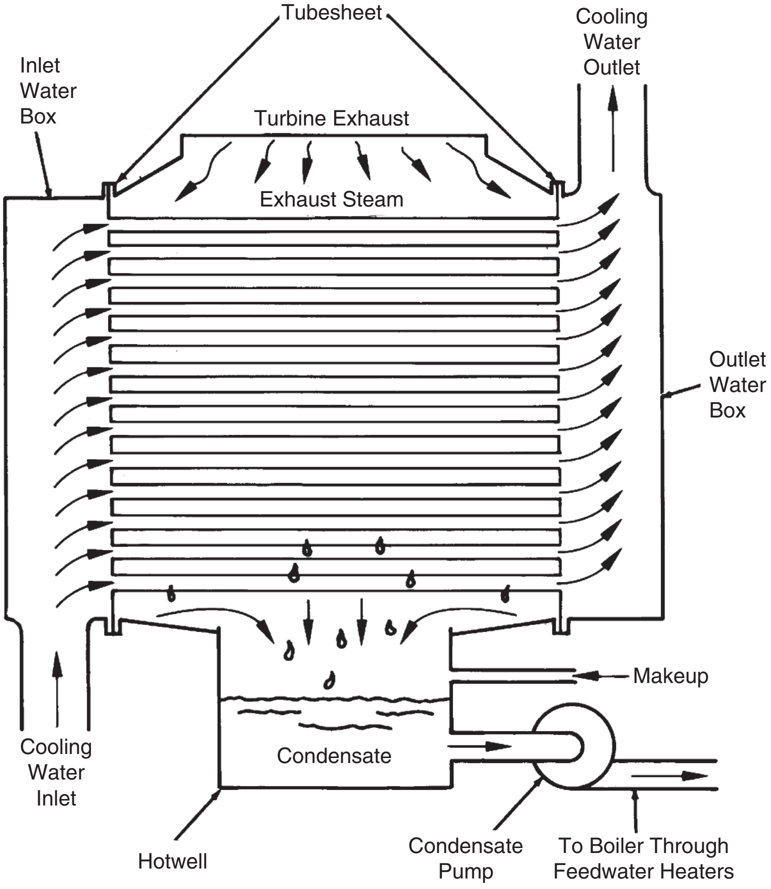


Figure 10.13 Basic surface condenser (side view).

Turbine condensers in high-pressure power plants are normally very efficient in reducing noncondensables (including oxygen) in the steam condensate, when operating at full load with less than 3% makeup and low air inleakage. However, during low-load operations:

- Condenser air inleakage rates increase as more equipment operates under vacuum.
- The resultant increased vapor tends to overload the vent system at the same time as the vent system capacity is reduced at lower condenser pressures.
- Steam distribution deteriorates within the condenser as the reduced heat load allows the majority of the steam to be condensed in the outer peripheral tubes. Noncondensables are neither limited to nor concentrated in the center of the tube bundle, where the vacuum pump suction piping is normally located.
- Condensate subcooling increases as the heat load is reduced.
- Condensers become less effective in deaeration.

At loads other than full load, deaeration efficiency can be improved by installation of a steam bubbler deaerator in the hotwell. This device is similar in some respects to the steam scrubber in a spray deaerator.

In combined cycle heat recovery steam generation (HRSG) plants, where the percentage of makeup water is higher than in conventional power plants, some plants have been retrofitted with vacuum deaerators that treat all makeup water using steam from the condenser. The deaerated makeup is added to the condensate from the condenser tubes and falls into the hotwell.

Feedwater Tanks

Feedwater tanks are typically installed in low-pressure plants [usually less than 100 psig (689 kPag)] that are not equipped with deaerators or some other type of deaerating equipment. Some manufacturers promote them for use with firetube boilers or commercial hot water heaters.

The feedwater tank serves multiple needs. It is used as a hot condensate receiver, cold water makeup addition point, feedwater heating vessel, deaerator, hot feedwater storage reservoir, and feedpoint for various chemical treatments.

The design and construction of feedwater tanks is often poorly done by people with inadequate training or experience. Bad design and poor operational practices lead to a number of problems, especially corrosion. Some poor design and operating practices include:

- There is no supplementary form of heating provided to the tank, so temperature varies depending on percent condensate return.
- The feedwater tank receives minimal condensate return and is cold.
- The oxygen scavenger cannot cope with the high volume of cold feedwater, and chemical deaeration is poor.
- The feedwater tank is undersized, and oxygen scavenger contact time is limited.
- Catalyzed oxygen scavenger is fed in conjunction with phosphates, chelants, or polymers, which consume the catalyst and thus decrease reaction rate.
- The scavenger feedpoint does not provide good mixing or distribution throughout the tank, contact time is limited, and scavenger consumption is higher than expected.
- Short-circuiting between the cold makeup inlet and the feedwater outlet reduce scavenger contact time.

Boiler systems relying on such poorly designed or operated feedwater tanks suffer rapid and extensive oxygen corrosion in the feedwater tank, feedwater line, boiler (firetube or hot water), steam condensate equipment, and condensate return system. With poor oxygen removal, heavy pitting and tuberculation are often found on the boiler tubes and at the waterline of the feedwater tank and boiler shell.

Figure 10.14 shows a well-designed feedwater tank. Design considerations for a well-designed feedwater tank should include the following:

- Feedwater tank should be maintained at a constant temperature above 185°F (85°C), ideally above 195°F (91°C), with a supplementary steam sparge, if needed.
- Returned condensate should be discharged through a sparge pipe to the lowest practical point in the feedwater tank. The cold makeup water supply line should also incorporate a sparge pipe but should be positioned at the highest practical point. This arrangement avoids poor water mixing because of stratification.
- The feedwater tank must be adequately vented. Typically, the vent pipe diameter should increase by l inch for every 120 to 150 gal (25 mm for each 0.5 m^3), and two vents are required for tanks larger than 650 gal (2.5 m^3).

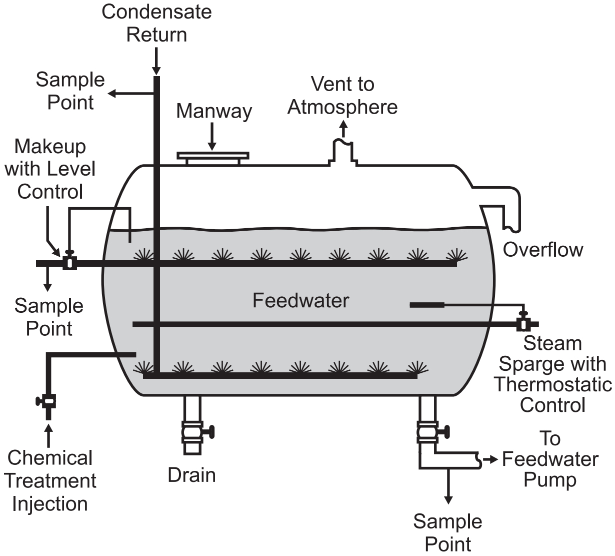


Figure 10.14 Properly designed feedwater tank.

- The tank should be large enough to hold a 1-hour supply of feedwater at maximum steaming rate.
- The tank should also be large enough to accommodate peak returns and surges of condensate, as well as shortfalls in makeup water supply caused by softener regeneration problems.
- The tank should be positioned sufficiently high off the floor to ensure that the feedwater pumps are provided with sufficient NPSH, so that they do not cavitate at the desired operating temperature.
- Sample points should be provided for the final feedwater and all sources of water, steam, and condensate that supply the feedwater tank. All feedwater tank sample points should incorporate a sample cooler.

Many manufacturers may not comply with these standards unless required to do so. Even this system with all items as specified will not result in complete removal of all oxygen. However, it will reduce oxygen better than many poorly designed systems in operation today.

Corrosion protection of the tank from oxygen is optional and may consist of baked epoxy linings or stainless steel.

Due to the inefficiency of feedwater tanks in removing dissolved oxygen mechanically, the chemical scavenger used must be catalyzed sodium sulfite. In addition, appropriate alkalinity, pH, time, and temperature conditions must be provided. Product stoichiometry up to five times theoretical may be required. Additional caustic feed may be necessary to counteract the boiler water alkalinity consumption when using liquid bisulfite, which is acidic.

Measuring the desired feedwater or boiler water scavenger residuals never guarantees that all oxygen has been removed. Residual oxygen and scavenger can and do exist together in the system if scavenging conditions are not optimal. Since oxygen is extremely volatile, any dissolved oxygen entering the boiler will release into the steam.

As with deaerators, routine dissolved oxygen testing in the boiler feedwater is critical to assure good corrosion control.

Gas Transfer Membranes

Membranes have been used to degasify water for a number of years in laboratory environments; however, it is only since about 1993 that they have become commercially feasible for industrial systems. The membrane unit design in use today is capable of flow rates up to 400 gpm (91 m^3/h).

Membrane degasification modules are called membrane contactors. They are usually shell-and-tube devices with water on the shell side and gas or vacuum on the tube side. A typical membrane contactor contains thousands of microporous polyolefin hollow fibers (tubes) woven into a fabric array that is wound around a central distribution tube with a central baffle (see Fig. 10.15). Since the

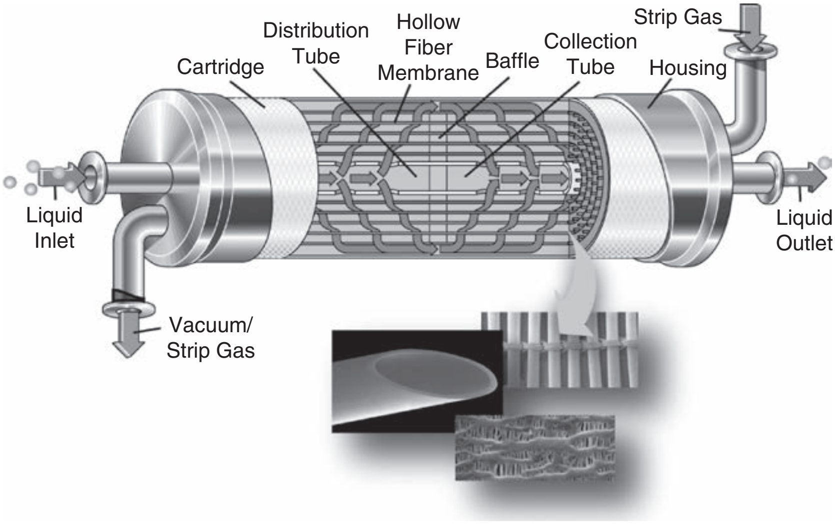


Figure 10.15 Liqui-Cel® membrane contactor. (*The illustration of the Liqui-Cel® Extra-Flow Membrane Contactor is provided by Membrana. Liqui-Cel® is a registered trademark of Membrana-Charlotte, A division of Celgard LLC.*)

membrane is hydrophobic, it will not let the liquid pass through the pores into the gas side. It essentially acts as a support between the gas and liquid phases that allows them to interface at the pores. By adjusting the partial pressure of the gas in contact with the water, gases can be selectively removed (or dissolved) into the water.

Water flows radially across the membrane, which induces local turbulence and increases diffusion to the membrane surface in the water phase. Since a membrane contactor contains many small diameter fibers, the interface area between the gas and liquid is very high. In fact, the contact area per unit volume ratio is typically an order of magnitude greater than that for a conventional packed column.

Gas transfer membranes operate with the same principles that govern the operation of a vacuum deaerator or conventional degasification column. If the partial pressure of the gas in contact with the water is reduced, the amount of gas dissolved in the water will be reduced correspondingly. The partial pressure of the gas can be lowered in two ways:

1. The total pressure of the gas phase can be lowered by imposing a vacuum to the gas side of the membrane.
2. The concentration of gases in the gas phase can be altered by using a strip gas that contains little or none of the gas being removed.

Membrane contactors will often use a combination of these two methods to achieve best results. Vacuum requirements may vary with temperature, but 27 inches Hg (686 mm Hg) at 72°F (22°C) is typical.

The degree of oxygen removal varies with temperature and gas evacuation method. Over a range of 55 to 77°F (13–25°C), effluent dissolved oxygen concentration may range from 1.3 to 0.6 mg/L. Typical oxygen removal rates range from 87 to 94% with combined vacuum and nitrogen sweep, falling to 83% with either nitrogen sweep or vacuum alone.

The internal (shell side) pressure drop of a 250 gpm (0.95 m^3/min) contactor operating at maximum capacity is less than 6 psig (41 kPag), allowing these devices to be placed in series for an overall efficiency increase. For example, if three contactors were placed in series and operated under normal conditions, the first contactor would remove 95% of the oxygen, the second contactor would remove 95% of the remaining oxygen, and the third contactor would remove an additional 95% of the remaining oxygen. Starting with 8.5 mg/L O_2 (8500 μg/L), a final dissolved oxygen concentration less than 15 μg/L could be obtained. Up to five contactors can be piped in series to achieve residual oxygen levels below 1 ppb.

The membrane can remove a variety of gases from water, but they must be volatile (present as a dissolved gas), and they must exert a partial pressure. Carbon dioxide is more difficult than oxygen to remove because of its ability to be present in several forms. Only free carbon dioxide (CO_2) is removed, not the bicarbonate (HCO_3^-) or carbonate (CO_3^{-2}) forms.

Carbon dioxide removal may vary from 90% at a pH of 4.9 to 70% at a pH of 5.3. Temperature has a decided effect on carbon dioxide removal with 20 to 60% removal at 54 to 58°F (12–14°C), increasing to 70 to 90% removal at 59 to 75°F (15–24°C). As with oxygen removal, carbon dioxide removal varies with the extraction method. Combined vacuum and nitrogen sweep improves carbon dioxide removal. Even though carbon dioxide removal may be incomplete, the residual CO_2 present in the effluent of a gas membrane contactor will be lower than can be achieved by a forced-draft atmospheric decarbonator. These membrane devices are warranted to 1 ppm of CO_2 while a forced draft atmospheric decarbonator will typically produce effluent water with 7 ppm CO_2.

The membrane contactors have an upper temperature limitation of approximately 140°F (60°C). However, there are fiber variants that can withstand temperatures as high as 185°F (85°C).

Some makeup water treatment plants combine membrane technology with conventional ion exchange polishing or electrodeionization (EDI) technologies. Gas removal is practiced upstream to reduce the ion exchange loading on the anion resin as well as protect the resins from oxidation. Degassed high-purity water can then be stored in lower cost storage tanks, operated with a nitrogen blanket.

The recommended pretreatment ahead of gas transfer membranes to prevent fouling by organics, colloids, and particulates, is filtration down to 10 micron or reverse osmosis (RO). Major components in the operating cost for this system are likely to be membrane maintenance and replacement, along with vacuum pump operation and maintenance.

Activated Carbon Catalysis

The chemical reaction between dissolved oxygen and hydrazine is well known and proceeds very slowly at ambient temperature and neutral pH.

$$N_2H_4 + O_2 \rightarrow 2H_2O + N_2 \tag{10.5}$$

Application of dosages in excess of 300% stoichiometric and contact times over two hours may not result in complete oxygen removal. The use of catalyzed hydrazine, either metallic or organic in nature, at large excess dosages does not increase reaction rates appreciably for low-temperature applications [35–80°F (1.7–27°C)].

A number of patents exist from the mid 1980s for the catalysis of hydrazine and other oxygen scavengers (carbohydrazide, diethylhydroxylamine, and erythorbic acid) by activated carbon. The process involves the addition of scavenger to water, passing the mixture through activated carbon media, followed by ion exchange downstream to remove any impurities added by the carbon bed.

Only the reaction with hydrazine is discussed here, although the other patented scavengers have been used successfully.

Water and hydrazine are intimately mixed before passing through a bed of activated carbon. The reaction is catalyzed by the activated carbon, reaching completion in a matter of seconds and at dosages approaching stoichiometry. Oxygen residuals below 25 μg/L can be obtained, if sufficient contact time is provided in the carbon bed. This typically requires volumetric flow rates less than 2.5 gpm/ft^3 (20 m^3/[h · m^3]). On a continuous basis, flow rates as low as 0.5 to 1 gpm/ft^3 (4–8 m^3/[h · m^3]) may be required. Laboratory data show that influent pH may also be important; however, commercial experience contradicts this with low oxygen effluent obtained within the operating pH range of 5.5 to 10.

Theoretically, there is no need to overfeed hydrazine since the activated carbon will allow stoichiometric reaction. In practice, however, a 10 to 20% hydrazine excess is recommended to allow for small changes in flow rates, dissolved oxygen content, and pumping inaccuracy. The stoichiometric ratio of hydrazine to oxygen is 1:1 on an active weight basis, that is, 1 mg/L active hydrazine should scavenge 1 mg/L O_2 in the presence of activated carbon.

Special grades of activated carbon are not apparently needed, but finer particles provide more surface area for the catalytic reaction than do coarser particles. Care must be taken to avoid particles and grades of carbon that can be lost during backwash.

There are many types of activated carbon, which may be petroleum based or made from materials such as coconut shells. The ash content of such carbons varies considerably, and the industrial and commercial demand for activated carbon sometimes causes extreme shortages of low-ash carbon. However, even low-ash carbon leaches undesirable impurities into the deoxygenated water. With some carbon materials, leaching declines slowly but in others continues at high concentrations for considerable time. When carbon must be replaced, it is frequently found the original low-ash material is not available, and substitute carbon may leach much higher contaminants.

For these reasons, this process must precede polishing treatment such as demineralization for removal of the ionic salt leachates and carbon fines. The amount of silica leached from the carbon may be significant and may require a downstream strong-base anion resin in the hydroxide form for removal. In most instances, a properly regenerated mixed-bed system downstream of the activated carbon media has been sufficient to deal with the leachables.

Lastly, care must be exercised in the design of a storage system that eliminates possible contamination of the effluent after deoxygenation. A floating bladder and nitrogen blanket systems are common approaches.

Ion Exchange Resin Catalysis

This system is often referred to as the catalytic oxygen removal system or CORS. It is similar in many respects to the activated carbon system described previously.

One version of this process uses a palladium coated, strong-base anion exchange resin as the catalyst and hydrogen or hydrazine to react with the oxygen. Residual oxygen in the deoxygenated water can be less than 2 μg/L with stoichiometric dosage of chemical.

This process has also been successfully tested using either hydroxide form strong-base anion resin or anion rich mixed-bed demineralizers with hydrazine or carbohydrazide for the chemical scavenger. Chemical dosage requirements may be two to three times the stoichiometric amount required for the oxygen concentration.

If hydrazine is used, the anion resin need not be regenerated unless other contaminants are present in the water. If carbohydrazide is used, periodic regeneration may be required, because the reaction of carbohydrazide with oxygen produces carbon dioxide that will be removed by the anion resin. In addition, excess hydrazine may be removed using a hydrogen form strong acid cation unit or left in the water to prevent reoxygenation.

Since unit flow rates affect the contact time, they are extremely important to the final oxygen concentration achieved. However, very little data have been published to date for good guidance in this area.

Chemical Oxygen Scavengers

Many pressure deaerators are capable of reducing the oxygen level to less than 10 μg/L. However, considering the corrosive potential of oxygen, it is best to remove all traces of oxygen. This is accomplished with chemical oxygen scavengers that react with the free oxygen to form harmless oxidized products. The reaction products are subsequently removed through boiler blowdown or system venting. Chemical oxygen removal is the last opportunity to prevent oxygen from entering the boiler.

For these scavengers to be effective in protecting the metal surfaces of a boiler system, they must be correctly applied and mixed with the boiler feedwater. The need to protect the system starts at the deaerator or feedwater tank.

Deaerators furnished with separate deaerating vessels mounted on separate storage vessels, have one or more interconnecting legs that act as water downcomers and steam equalizing pipes. In such cases, the preferred scavenger injection point is into the water downcomer between the vessels, using a special injection quill to get maximum mixing. Care must be taken to ensure the water downcomer is used for this purpose and not a steam equalizer.

For units without separate deaerating domes or water downcomers, it is recommended that the scavenger be fed into the storage tank below the water line. A single injection point at either end or into the middle provides poor scavenger and water mixing and often fails to provide sufficient contact time for the reaction with oxygen, especially when equipment stops functioning properly. The recommendation for scavenger feed into the storage section is either to feed into both ends or through a modified header type arrangement that distributes chemical across the entire storage section (see Fig. 10.16).

There are several commercially available oxygen scavengers in the market place today:

- Sulfite (Na_2SO_3)
- Hydrazine (N_2H_4)
- Carbohydrazide [$(NH_2NH)_2CO$]
- Erythorbate ($RC_6H_6O_6$ where R is H^+, Na^+, or amine)

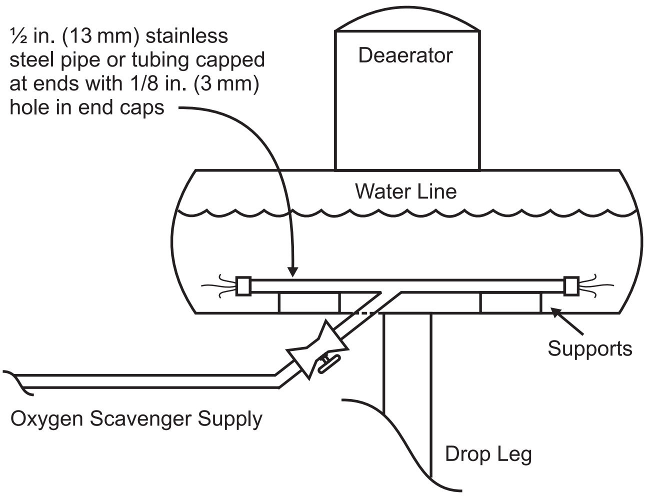


FIGURE 10.16 Alternative oxygen scavenger feed point. The arrow indicates a ½ inch (13 mm) stainless steel pipe or tubing capped at the ends with 1/8 inch (3 mm) hole in the end caps.

- Diethylhydroxylamine [$(C_2H_5)_2NOH$]
- Methylethylketoxime (C_4H_8NOH)
- Hydroquinone [$C_6H_4(OH)_2$]

Each scavenger has slightly different characteristics. In actual systems, the effectiveness of oxygen scavengers can depend on many thermodynamic and kinetic factors:

- Scavenger concentration, type, and variability
- Dissolved oxygen concentration and variability
- Time for the chemical reaction
- pH of the water
- Temperature of the water
- Presence of catalysts
- System metallurgy (brass, copper, carbon steel, etc.)
- Other chemical species in the water

Sodium Sulfite (Na_2SO_3)

For many industrial boiler applications, sodium sulfite is an easily controlled oxygen scavenger. Table 10.1 shows typical boiler water sulfite residuals carried at various operating pressures.

Sodium sulfite reacts directly with dissolved oxygen.

$$2Na_2SO_3 + O_2 \rightarrow 2Na_2SO_4 \tag{10.6}$$

Approximately 8 mg/L of pure sodium sulfite is required to react with 1 mg/L of dissolved oxygen.

Sodium sulfite can be catalyzed or uncatalyzed. Reaction rates of both catalyzed and ordinary sodium sulfite increase with temperature. Even at typical deaerator outlet temperatures of 210 to 250°F (99–121°C), catalyzed sulfite is preferred to uncatalyzed sulfite for the very short reaction time available in boiler feedwater systems.

Boiler Pressure, psig (MPag)	Sulfite Residual, ppm SO_3^{-2}
up to 150 (1.0)	30–60
150–300 (1.0–2.1)	30–40
300–600 (2.1–4.1)	20–30
600–900 (4.1–6.2)	10–15
above 900 (6.2)	not recommended

TABLE 10.1 Typical Boiler Water Sulfite Residuals at Various Operating Pressures

Reaction time is an important consideration. The corrosive reaction of oxygen with wetted steel surfaces at feedwater temperatures above 300°F (150°C) will be faster than the reaction between sulfite and oxygen. It is imperative that the oxygen is chemically scavenged before the feedwater reaches high-temperature heaters, economizers, or the boiler metal itself. To avoid releasing corrosive oxygen into the steam, the oxygen must be chemically reduced before the feedwater enters the boiler drum.

Cobalt salt, a commonly used catalyst, speeds the reaction of sulfite at low temperatures. A drawback is that this catalyst can be deactivated or precipitated by the presence of phosphates, phosphonates, chelates, polymers, or solutions of pH 9 or higher.

Following are some disadvantages associated with using sodium sulfite:

- Sodium sulfite adds solids to the boiler water. This may contribute to an increased blowdown requirement. Blowdown is a direct loss of energy and increased water treatment costs.
- Sodium sulfite cannot be used in spray attemperation applications, because the solids contribution of sodium sulfite would cause superheater and turbine deposits. In addition, since sodium sulfite must be fed after the attemperation take-off point, all equipment upstream of that point would be subject to oxygen corrosion and costly repairs unless stainless steel is used. Additionally, when feeding sulfite after the attemperation water take-off, the available reaction time between the oxygen and the scavenger is greatly reduced.
- The decomposition of sulfite to corrosive gasses of hydrogen sulfide (H_2S) and sulfur dioxide (SO_2) begins at a pressure of approximately 600 psig (4.1 MPag). For this reason, the use of sulfite as an oxygen scavenger is not recommended above 900 psig (6.2 MPag).
- Sodium sulfite acts primarily as an oxygen scavenger; it is not generally recognized as a metal passivating agent.
- Overfeed or high dosages of liquid sodium bisulfite can result in acidic conditions in both the feedwater and boiler equipment. This most commonly occurs with a malfunctioning deaerator, when the tendency is to continuously increase scavenger feed in the attempt to maintain a residual.

Additionally, sodium sulfite (or liquid sodium bisulfite) is not recommended for the following applications:

- Boiler systems using coordinated phosphate programs
- Condensate systems (sulfite is not volatile and will add solids to the condensate)

- Lay-up or cold storage of nondrainable superheaters (sulfite will add solids to the water, resulting in superheater deposits)

The use of sulfite as a feedwater oxygen scavenger is an industry-wide practice that generally does not cause problems when used under established guidelines. However, if the dissolved oxygen is high and an insufficient amount of sulfite is fed to react with all of the oxygen, the presence of sulfite in highly oxygenated water can exacerbate pitting.

Hydrazine (N_2H_4)

Hydrazine can be used at all operating pressures and where feedwater is used for steam attemperation. Hydrazine reacts directly with oxygen.

$$N_2H_4 + O_2 \rightarrow 2H_2O + N_2 \tag{10.7}$$

The direct reaction with oxygen proceeds relatively slowly at temperatures below 300°F (150°C). However, the rate is highly sensitive to the presence of both homogeneous (soluble) and heterogeneous (insoluble) catalysts. For example, the reaction of hydrazine with oxygen can proceed at an acceptable rate at temperatures as low as 150°F (65.6°C) in the presence of heterogeneous catalysts such as the surface of mild steel or copper. A proposed mechanism for this catalysis utilizes the following overall reactions:

$$4Fe_3O_4 + O_2 \rightarrow 6Fe_2O_3 \tag{10.8}$$

$$6Fe_2O_3 + N_2H_4 \rightarrow 4Fe_3O_4 + 2H_2O + N_2 \tag{10.9}$$

In the presence of copper or its alloys, the reactions proceed as follows:

$$2Cu_2O + O_2 \rightarrow 4CuO \tag{10.10}$$

$$4CuO + N_2H_4 \rightarrow 2Cu_2O + 2H_2O + N_2 \tag{10.11}$$

At boiler water or steam temperatures above 400°F (204°C), hydrazine begins to decompose to form ammonia, nitrogen, and sometimes hydrogen by either or both of Eqs. 10.12 and 10.13. By 600°F (316°C), hydrazine is virtually gone.

$$3N_2H_4 + \text{heat} \rightarrow 4NH_3 + N_2 \tag{10.12}$$

$$N_2H_4 + \text{heat} \rightarrow N_2 + 2H_2 \tag{10.13}$$

Hydrazine also enhances metal passivation.

Some hydrazine products are available in the catalyzed form. Tests have shown that catalyzed hydrazine is a more effective oxygen scavenger at temperatures well below those found in feedwater and boiler systems, but shows no significant advantages at elevated temperatures.

Hydrazine also has drawbacks:

- One of the decomposition products of hydrazine is ammonia (NH_3). Ammonia will increase the corrosion rates of copper and copper alloys in the presence of oxygen.
- Hydrazine is a suspect human carcinogen; therefore, it should be handled with the least exposure possible. Closed feeding systems should be used to eliminate exposure. Studies have shown that when hydrazine is handled in closed or ventilated systems, the levels can be controlled to less than 0.1 mg/L in air.
- At low temperatures, hydrazine is slow to react. If, as in some utilities, hydrazine is fed to the condensate hotwell, very high dosages are necessary to protect the system fully. Slow reaction time means the possibility of oxygen attack, even with hydrazine in the system.

Carbohydrazide [$(NH_2NH)_2CO$]

The concerns associated with handling hydrazine prompted the development of an alternative. The product developed, carbohydrazide, can be used in all types of boilers. Although it is not volatile, all of its decomposition, hydrolysis, and reaction products are, so carbohydrazide is often referred to as an all-volatile chemistry.

The reaction of carbohydrazide with oxygen is similar to that of hydrazine but more complex. Carbohydrazide treatment provides numerous intermediary reactions that increase the reactivity of the product and can provide improved metal passivation. At temperatures below 275°F (135°C), carbohydrazide reacts directly with oxygen.

$$(NH_2NH)_2CO + 2O_2 \rightarrow 2N_2 + 3H_2O + CO_2 \qquad (10.14)$$

This makes carbohydrazide a useful oxygen scavenger as well as metal passivator for feedwater systems (deaerators, economizers, etc.).

At temperatures above 275°F (135°C), carbohydrazide begins to hydrolyze to form hydrazine and carbon dioxide (CO_2).

$$(NH_2NH)_2CO + H_2O \rightarrow 2N_2H_4 + CO_2 \qquad (10.15)$$

As the temperature increases further, the hydrazine formed from the carbohydrazide decomposes, as discussed earlier.

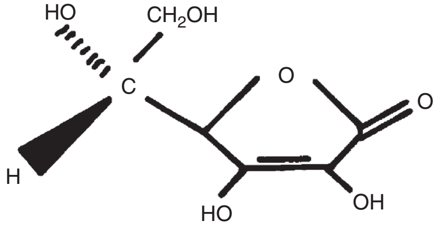
Carbohydrazide is unique because one of the breakdown products is hydrazine. This means that at higher temperatures, carbohydrazide continues to scavenge oxygen and passivate metal surfaces. Above 400°F (204°C), hydrazine begins to decompose to ammonia, nitrogen, and water, none of which adds significant conductivity to the boiler water.

Erythorbate ($RC_6H_6O_6$ Where R Is H^+, Na^+, or Amine)

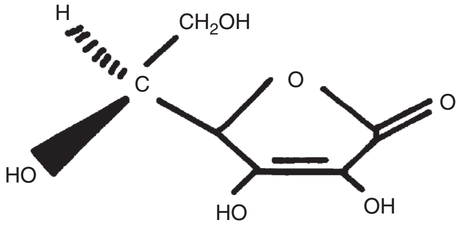
The erythorbate-based oxygen scavenger is a nonvolatile organic chemical reducing agent designed to scavenge oxygen and enhance passivation of metal surfaces. Similar to L-ascorbic acid (vitamin C), D-erythorbic acid has been used since 1980 as a boiler water oxygen scavenger. Typically, erythorbic acid is neutralized with either an amine or sodium hydroxide. Where the acid is neutralized with amine, the product may be used in boiler feedwater used for steam attemperation, because the product decomposes to gases at elevated temperatures. Where the acid is neutralized with caustic, the product should not be used in attemperation water, because the sodium salts will deposit on superheater tubes and turbine blades. Figure 10.17 shows the chemical structure of these compounds.

The reaction of erythorbate with dissolved oxygen is complex, and the complete mechanism is not yet known. However, the overall reaction occurs as follows (R represents the preferred amine form):

$$RC_6H_6O_6 + \tfrac{1}{2}O_2 \rightarrow RC_6H_4O_6 + H_2O \tag{10.16}$$



D-Erythorbic Acid



L-Ascorbic Acid

Figure 10.17 Chemical structures of D-erythorbic acid and L-ascorbic acid.

Erythorbate does not contribute solids to boiler water. At elevated temperatures [500°F (260°C)], erythorbate decomposes to CO_2 and water.

Amine-neutralized erythorbate can be used for spray attemperation, because it breaks down to the volatile components of carbon dioxide and water under attemperation conditions. Field studies demonstrate that erythorbic acid does not contribute to turbine deposits. The unique chemistry of erythorbate permits it to be added upstream of the spray attemperation take-off point. Because it can be added at an earlier point in the feedwater system, more of the equipment can be protected from oxygen attack.

Because erythorbate begins to thermally decompose at deaerator temperatures, overfeed or relatively high dosages can result in acidic conditions in both the feedwater and boiler equipment. This most commonly occurs with a malfunctioning deaerator, when the tendency is to continuously increase scavenger feed in the attempt to maintain a residual.

Diethylhydroxylamine [$(C_2H_5)_2NOH$]

Diethylhydroxylamine (DEHA) has been used in boiler water treatment since 1981. DEHA is both an oxygen scavenger and a metal passivator. However, Nalco research suggests hydrazine, carbohydrazide, and erythorbate are better oxygen scavengers, reductants, and metal passivators than DEHA.

Being an amine, DEHA acts as a typical neutralizing amine ($pK_a = 8.3$). In systems using DEHA, the neutralizing amine feed rate can often be reduced. DEHA has a volatility distribution ratio similar to that of many neutralizing amines. Since it is volatile, DEHA can be fed to the preboiler system and provide protection throughout the entire boiler system, including the condensate system. DEHA does not add solids to water; therefore, DEHA can be used in steam attemperation water. Its amine characteristics (basicity and volatility) are among the most attractive features of DEHA.

The reaction of DEHA with dissolved oxygen is complex and appears to generate intermediates, which are further oxidized at higher temperatures. The reaction rate is dependent on pH, temperature, and the ratio of DEHA to dissolved oxygen. Theoretically, DEHA reacts with oxygen as follows:

$$4(C_2H_5)_2NOH + 9O_2 \rightarrow 8CH_3COOH + 2N_2 + 6H_2O \tag{10.17}$$

In practice, the reaction does not proceed stoichiometrically to acetic acid as shown in Eq. (10.17). The first-stage reaction is believed to produce a nitrone as shown in Eq. (10.18).

$$(C_2H_5)_2NOH + \tfrac{1}{2}O_2 \rightarrow C_2H_5NOCH_3CH + H_2O \tag{10.18}$$

The nitrone is further oxidized to acetaldoxime as shown in Eq. (10.19).

$$C_2H_5NOCH_3CH + \tfrac{1}{2}O_2 \rightarrow CH_3CHNOH + CH_3CHO \qquad (10.19)$$

When sodium hydroxide is present in the boiler water, the acetic acid produced is trapped as sodium acetate and removed by continuous blowdown. The other reaction products are volatile and exit the boiler with the steam. The autodecomposition temperature for DEHA starts at 255°F (124°C), and by 400°F (204°C), there is no DEHA remaining. In systems with superheat, additional DEHA might be needed after the superheater to assure complete protection.

As an organic compound, DEHA has the potential to cause the same acidic problems in feedwater and boiler equipment due to overfeed or high dosages as erythorbate, methylethylketoxime, and hydroquinone. This most commonly occurs with a malfunctioning deaerator, when the tendency is to continuously increase scavenger feed in the attempt to maintain a residual.

DEHA quickly degrades as the pressure increases above 240 psig (1.7 MPag). The major degradation product appears to be diethylamine, a volatile neutralizing amine that will contribute to pH control in the steam condensate system. Some ammonia may also be formed.

DEHA will react with iron and copper oxides to form passive metal films as shown in Eqs. 10.20 and 10.21.

$$(C_2H_5)_2NOH + 6Fe_2O_3 \rightarrow 4Fe_3O_4 + CH_3CHNOH + CH_3CHO + H_2O \qquad (10.20)$$

$$(C_2H_5)_2NOH + 4CuO \rightarrow 2Cu_2O + CH_3CHNOH + CH_3CHO + H_2O \qquad (10.21)$$

In commercial products, DEHA is generally blended with other materials. In oxygen scavenger formulations, DEHA is typically blended with hydroquinone, which improves oxygen scavenging at low temperatures. In condensate system formulations, DEHA can be blended with various neutralizing amines.

Methylethylketoxime (C_4H_8NOH)

Methylethylketoxime (MEKO) was patented as an oxygen scavenger in boiler systems in 1984. The reaction with oxygen is virtually nonexistent at room temperature without a catalyst and is independent of solution pH, which is unusual for an oxygen scavenger. The reaction of MEKO with oxygen produces only volatile reaction products [methylethylketone (MEK), nitrous oxide, and water] as shown in Eq. (10.22).

$$2CH_3CH_3CH_2CNOH + O_2 \rightarrow 2CH_3CH_3CH_2CO + N_2O + H_2O \tag{10.22}$$

Above 572°F (300°C), MEKO decomposes to MEK, nitrous oxide, nitrogen, ammonia, and carbon dioxide. Since all of these materials are volatile, MEKO can be used in steam attemperation water.

Like DEHA, MEKO is volatile and protects the postboiler system when fed to the preboiler equipment. However, in systems with superheaters, additional MEKO should be added after the superheaters to assure complete coverage and protection. MEKO has a volatility distribution ratio between that of diethylaminoethanol and cyclohexylamine.

Proponents of MEKO claim it reacts with iron and copper oxides to form passive metal films. The suggested pathways are shown in Eqs. 10.23 and 10.24.

$$2CH_3CH_3CH_2CNOH+6Fe_2O_3\rightarrow 4Fe_3O_4+2CH_3CH_3CH_2CO+N_2O+H_2O \tag{10.23}$$

$$2CH_3CH_3CH_2CNOH + 4CuO \rightarrow 2Cu_2O + 2CH_3CH_3CH_2CO + N_2O + H_2O \tag{10.24}$$

As MEKO reacts and degrades, it generates ammonia. At 1800 psig (12.4 MPag), MEKO will produce the same amount of ammonia as would be generated from an equivalent amount of nitrogen in the form of hydrazine.

Literature shows that MEKO does not always react with oxygen to completion, even in the presence of copper, and the reaction may be only 60 to 70% complete. MEKO, like DEHA, is a slow oxygen scavenger at low temperatures. The hydrolysis of MEKO to hydroxylamine produces the scavenging ability noted for this compound. At temperatures above 385°F (196°C), MEKO decomposes to organic acids and other species that have little or no value as oxygen scavengers.

In electric utility systems, MEKO and DEHA feed points are often to the shell side of the feedwater heaters. This is done to enhance scavenging (heat activation) due to the negligible scavenging by these chemistries at low temperatures.

Like erythorbate, DEHA, and hydroquinone, MEKO has the potential to cause acidic problems in both feedwater and boiler equipment due to overfeed or high dosages. This most commonly occurs with a malfunctioning deaerator, when the tendency is to continuously increase scavenger feed in the attempt to maintain a residual.

Hydroquinone [$C_6H_4(OH)_2$]

Hydroquinone (HQ) was first used in boiler water applications as an additive in hydrazine solutions, forming "catalyzed" hydrazine. Today, products can be found using HQ alone. HQ is also used in DEHA formulations to provide better oxygen scavenging at low temperatures.

The reaction rate between HQ and dissolved oxygen is dependent on temperature, solution pH, and the ratio of HQ to dissolved oxygen. The reaction proceeds quite vigorously even at low temperatures, which is why HQ is often used to enhance other oxygen scavengers. The HQ-oxygen reaction is quite complex and appears to involve multiple stages. Based on autoclave studies, the first-stage reaction is believed to yield benzoquinone as shown in Eq. (10.25).

$$C_6H_4(OH)_2 + \tfrac{1}{2}O_2 \rightarrow C_6H_4O_2 + H_2O \qquad (10.25)$$

The benzoquinone subsequently undergoes further reaction with dissolved oxygen to yield light alcohols and ketones as shown in Eq. (10.26).

$$C_6H_4O_2 + O_2 \rightarrow \text{light alcohols} + \text{ketones} + CO_2 \qquad (10.26)$$

Due to the secondary reaction [Eq. (10.26)], less than stoichiometric amounts of HQ are needed to successfully scavenge dissolved oxygen in boiler feedwater. Because the amount of HQ used in typical applications is small, the amount of reaction products is very low.

The reaction products between HQ and dissolved oxygen do not add solids to water; therefore, HQ can be used in attemperation applications.

In some low-pressure, high-purity boiler water applications, HQ can depress the boiler water pH below the desired set point. Neutralizing amines might not raise the boiler water pH, because the amines are volatile while HQ is not. In high-pressure applications, HQ is volatile and behaves like DEHA and MEKO, protecting the postboiler system.

HQ contains no nitrogen; therefore, HQ does not generate any ammonia.

Proponents of HQ claim it will passivate iron and copper oxides; however, the exact reactions are not fully understood.

One of the major drawbacks of hydroquinone is its toxicity; it is listed as a mutagenic and Class B poison.

Monitoring and Control

In the early part of the 21st century, steam plant management teams came to face a new series of challenges. The one thing that had not changed was the need to assure continuous steam flow to whatever process the facility needed for production. Moreover, the competitive nature of the global economy made cost-effective steam production even more important. However, other things were definitely changing. Fuel costs were increasing, sometimes rapidly, putting extreme budgetary pressure on utility costs. The workforce was changing, getting older in some cases, much less experienced in others, with headcount reduced at more plants, making previous operating strategies impossible to maintain. Finally, a new level of corporate involvement in plant operations was implemented, to oversee operations that were vital to survival of the parent company.

The boiler feedwater system is a frequently overlooked source of steam plant challenges. Water temperatures are not so high as to drive chemical reactions to instantaneous completion, but they are certainly accelerated over ambient conditions. Considering the boiler economizer as part of this system, fireside temperatures are not so high as to cause short-term or even long-term overheat failures. However, mechanical stresses cause a disproportionate amount of forced downtime. In addition, safety must be considered. Corrosion failure of a feedwater line can cause explosive release of water and steam into the surrounding work areas, and fatalities have resulted from these events. Therefore, the need for improvement in the operation, control, and maintenance of the boiler feedwater system is clear.

Previous operating strategies focused on maintaining boiler feedwater pH and dissolved oxygen concentration to maintain reliable system operation. Details of this are more fully described earlier in this chapter, but are focused on collecting a cooled sample of feedwater and using instruments to measure pH and oxygen and scavenger concentration. This type of measurement presents several problems when attempting to maintain on-line control. First and simplest, the process of sample cooling necessarily induces a lag time between when the sample was extracted from the feedwater line and when it is analyzed. In the case of an excursion or process event, this lag or delay can allow some period when the system is not controlled. Secondly, because the target for the desired dissolved oxygen concentration in boiler feedwater is 10 μg/L or less, any air intrusion into the sample could be interpreted as an excursion. The oxygen concentration in air is about 20%, while the desired concentration in feedwater is less than 10 μg/L. Therefore, even a very small influx of air during sampling is enough to suggest a serious event, when one is not actually occurring.

A new corrosion monitoring and control technology called AT ORP™ (At-Temperature Oxidation/Reduction Potential) has been developed to overcome weaknesses of previous tools. This online monitoring tool can minimize corrosion in industrial and utility boiler systems by measuring the net oxidation/reduction potential (ORP) of the hot water at actual feedwater operating temperatures and pressures. This eliminates both sample lag time concerns and potential for air intrusion as the sample is cooled, because the sample is never cooled for analysis. This technology detects subtle changes in oxidation/reduction stress, and responds in real-time by changing oxygen scavenger or passivator chemical feed to maintain a previously selected ORP set point. This makes it possible to detect and react to conditions inside the boiler system under actual operating temperatures and pressures, allowing the program to deliver superior boiler corrosion control. As part of a larger automation package, at temperature ORP provides continuous corrosion control and represents a paradigm shift in system monitoring and control.

Background

Reaction of oxygen with materials of construction used in boilers is the cause of many corrosion phenomena. This complex process depends on more than just the concentration of oxygen present, but also on factors such as water chemistry and metallurgy. For example, the presence of other chemical species in water could turn oxygen into a more aggressive corrodent. Other important factors include temperature, pressure, fluid velocities, and operational practices. While oxygen is often the primary or essential component in the corrosion process, it might not be the only one.

The conventional method to reduce oxygen corrosion in all industrial and even most utility water systems is to remove molecular dissolved oxygen by mechanical and chemical means. In a very few high-pressure boilers in electrical generating stations that use ultra high-purity water, a different approach has been taken. No oxygen scavenger is used, and in fact, small concentrations of oxygen are deliberately added to the feedwater. In this case, oxygen is used as an oxidant and acts as a passivating agent for carbon steel under carefully controlled conditions. More widely seen in Europe than North America.

Traditionally, the amount of oxygen scavenger fed to boiler feedwater has been based on knowing the amount of dissolved oxygen in feedwater plus some excess amount of scavenger. The amount of excess scavenger fed is based on the desired residual scavenger concentration in boiler feedwater or in boiler water itself. When the scavenger is sodium sulfite, boiler water residual is measured, because sulfite cannot be reliably detected at concentrations less than 5 mg/L, which it would be if a feedwater sample were analyzed. The nonsulfite group of scavengers, including carbohydrazide, ascorbic acid, DEHA, hydroquinone, and methylethylketoxime, are measured in boiler feedwater in the range of 100 μg/L or greater.

It is preferable that the operator knows the feedwater dissolved oxygen concentration without scavenger present. This is a way to assess operation of deaerator hardware to assure reliable performance. The dissolved oxygen concentration should be stable, or it should be measured regularly to make necessary chemical dosage changes. In many plants, chemical scavenger residual is the only parameter measured to assure prevention of oxygen corrosion. This can lead to feedwater system corrosion, because even though a scavenger residual is measured that does not mean all oxygen is scavenged in a timely manner. Kinetics of the reaction between low concentrations of oxygen and low concentrations of scavenger are such that complete removal should not be assumed.

Monitoring and Control Tools

Figure 10.18 shows some of the corrosion morphologies seen from oxygen attack. Massive pitting attack was seen while on sulfite

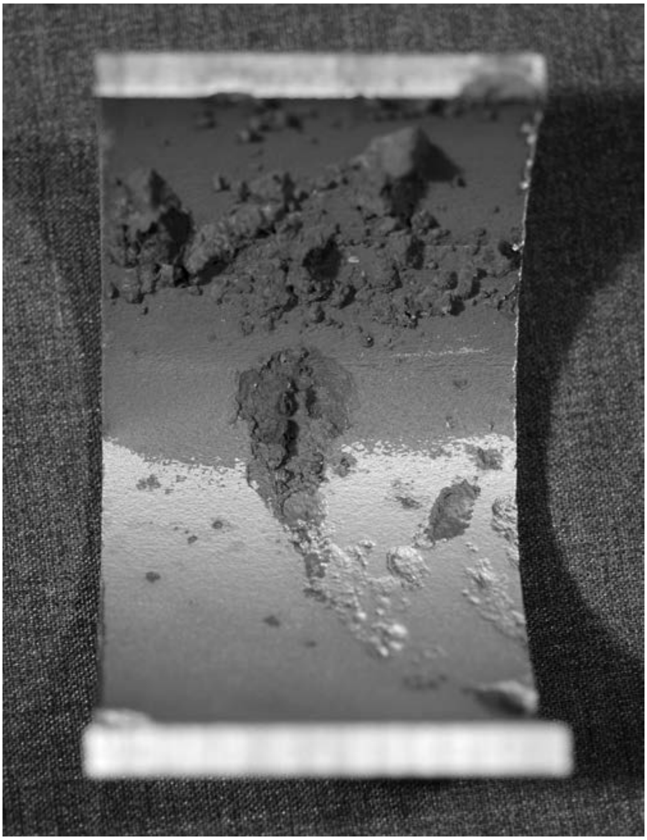


Figure 10.18 The top of the sample shows caps of iron oxide (tubercles) covering oxygen pit sites. Often a characteristic red oxide (hematite) is indicative of highly oxidizing conditions. The bottom of the sample shows the localized pitting of mild steel resulting from oxygen-induced corrosion (external corrosion product has been removed).

treatment (top side). In this case, insufficient sulfite was fed, leaving high dissolved oxygen conditions (>100 μg/L) with sulfate reaction products, which exacerbate localized pitting corrosion.

Performance of combined mechanical and chemical removal processes is often measured continuously using dissolved oxygen probes. Alternatively, dissolved oxygen studies can employ grab sample measurements, where a dye filled ampoule changes color based on oxygen concentration in the sample. Additionally, color change can be determined spectrophotometrically or with the naked eye through a comparator to correlate to a dissolved oxygen concentration.

Hence, there are several options, varying in sophistication and difficulty of use, to evaluate system performance. It is worth noting that no previous technology really measured conditions of metal surfaces where corrosion actually occurs. Rather, presence or absence of contaminants in the water stream flowing across the metal surface is measured, and the rate of potential damage to the surface inferred from the concentration of contaminant present.

There are various tools for feeding oxygen scavengers/metal passivators. Typical strategies for chemical scavenger feed include:

- Manual pump feed with drawdown calculations and periodic scavenger residual testing.
- Online scavenger residual determinations and control (e.g., online hydrazine analysis).
- Inert TRASAR® feed and control of scavenger products (concentration demand based off inert chemical formulated into product).
- Active TRASAR feed and control of scavenger products (concentration demand based off active chemical formulated into product).
- Feed scavenger off feedwater or steam flow (feed concentration demand).
- Feed chemistry based off timer.
- Slave feed of scavenger to other chemicals being controlled and fed into system or off other mechanical operations (e.g., turning boiler on and off).

Again, none of these feed schemes addresses true demand in real-time in any system, but they have been used with reasonable effectiveness as scavenger feed control schemes. Redox demand measured online at system temperature and pressure has been shown to relate more directly to the driving force or potential for a system to corrode.

Even when some of the best techniques for corrosion monitoring are applied, the very low general corrosion rates seen in boiler systems are difficult to discern. In addition, localized corrosion mechanisms are often occurring, not general corrosion, and the classic electrochemical monitoring tools provide little indication of localized corrosion. Trends in general corrosion can be useful, but are not applicable for use with automated control systems. In situ ORP monitoring overcomes these obstacles and provides a greater understanding of system performance.

Corrosion stresses and their impact on corrosion have been observed to be plant-specific, such as:

- System design and metallurgy
- Dissolved oxygen concentration (incipient and ingress)
- System pH
- Corrosion product concentration
- Temperatures and pressures
- Mechanical configuration and efficiency:
  - Deaerator tray alignment
  - Seal issues
  - Pump issues
  - Deaerator venting
  - Steam supply consistency
  - Condensate storage area integrity
- Seasonal variations in operating profile
- Ratio of condensate return to makeup water
- Changes in feedwater flow and steam load
- Reductant used (if any)
- Presence of specific catalysts to corrosion reactions
- Reductant residence times and concentrations
- Other chemical species (usually pH adjustments)
- Flow effects

While long, even this list is not all-inclusive. Hosts of other possible corrosion stresses exist, and because in situ ORP lends itself to assessing condition of the metal surface, it is the preferred monitoring and control parameter, avoiding need to assess each listed item and all interrelationships.

At-Temperature ORP Monitoring

A different approach from the traditional method of controlling reductants (such as oxygen scavenger feed) is based on redox potential of treated feedwater. ORP values are typically recorded between a noble metal electrode and a reference electrode (often platinum).

By measuring redox potential in situ, sample conditioning equipment can be eliminated. Sample system lag times are reduced, and potential for cooling water intrusion into the sample is avoided.

ORP has application wherever corrosion via oxidizing and reducing reactions is of concern. This involves all aqueous corrosion processes. Redox potential of feedwater is a function of dissolved oxygen concentration, oxygen scavenger concentration, and other factors (see Fig. 10.19). Measured ORP directly correlates with potential for systems to corrode. By targeting and maintaining specific redox potential in feedwater, it should be possible to feed the exact dosage of chemical additive required to protect a system from oxygen attack and minimize corrosion rates. The driving force for corrosion can now be controlled in real-time. Scavenger concentration varies based on redox demand. By constantly monitoring feedwater, it is possible to take immediate corrective action when there is a system change. Even in systems that do not feed reductants such as oxygen scavengers, in situ ORP technology still has application due to high sensitivity for detecting changes, which are then assigned to changing mechanical or operational parameters.

Many feedwater redox stress events are not predictable. Consequently, the majority of redox stress events go undetected, unnoticed, and thus uncorrected. Therefore, controlling redox stress in boiler

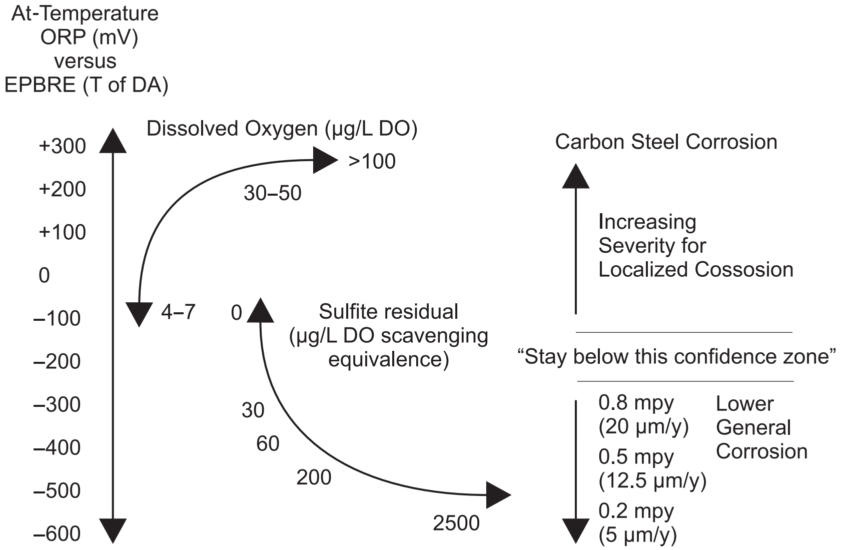


Figure 10.19 Schematic ORP correlation with oxygen, sulfite residual, and carbon steel corrosion implications, indicating why this system should be controlled under highly reduced conditions (low ORP zones).

feedwater is essential to maintaining integrity of boiler systems. Many years of excellent operation can be undone if short-term damaging events occur, especially when they are not detected and proper corrective measures are not taken.

Monitoring ORP has been found to be important in determining presence of electro-active redox species. ORP values reported are the net sum of redox potentials in the sample stream as measured on noble metals such as platinum or gold. It is important to know what potentials are being measured. Simply quoting ORP values without reference to the potential measured and reference electrode used can be very misleading. All conditions for measurement of ORP should be clearly stated, including temperature at which the measurement was taken. All in situ ORP measurements in this chapter were taken using an external pressure balanced reference electrode (EPBRE) filled with 0.1 N potassium chloride (KCl) and a platinum electrode.

ORP values measured against a reference electrode are thus relative numbers and need to be reported as such. Usually, these measurements are made against some standard reference electrode, like a silver/silver chloride electrode filled with potassium chloride. These measurements should be taken under representative conditions of temperature, pressure, and flow.

Flow rates are chosen so that representative water samples pass the electrodes. Ideally, conditions found in the electrochemical cell should mirror those found in bulk water in the system. The goal is to have a sample stream that is flowing “fast enough” to ensure chemical homogeneity of the sample with respect to the system at the point of sampling.

Measuring electrochemical potentials at low temperature and inferring behavior at higher system temperatures is usually misleading. Remembering that corrosion processes in steam systems change dramatically at elevated temperatures, what is of concern is measurement of electrochemical potentials at the system conditions of temperature and pressure.

There are many reasons why it is advantageous to measure ORP at temperature and pressure. Firstly, corrosion occurs in the system at temperature and pressure. Properties of core importance should thus be measured as close as possible to conditions at which critical corrosion processes occur. Active species should not be quenched to low temperature. Correlations at actual operating temperatures and pressures need to be captured. It is possible to see an effect at temperature that cannot be detected at lower temperatures, as equilibria can vary markedly with temperature.

The at-temperature sampling should be done earlier in the sample stream, so that response is rapid and representative of actual feedwater redox state. This is particularly relevant when sample streams can be sent to instrument panels far away from the point of sample extraction.

With oxygen scavengers, it is well known that they are more reactive at elevated temperatures. This is particularly true of many passivating scavengers like hydrazine, carbohydrazide, DEHA, etc. One reason for this is that the power of the reductant is enhanced at temperature, and thus, control based on reductant residual is more sensitive and realistic at temperature.

ORP measurement and control zones can be broadly represented as in Fig. 10.20. "DA + Scav" refers to the majority of systems with a deaerator and an oxygen scavenger/metal passivator. "+Cu" shows that to maintain low corrosion rates of copper alloys (as compared to carbon steel), a different ORP control zone is preferred. "OWT" applies to those systems practicing oxygenated water treatment. These types of systems, where small amounts of oxygen are purposefully added to feedwater systems to lower corrosion rates of iron-based metallurgies, apply only to a few electric utility-based systems. Systems using all volatile treatment (AVT) without scavenger typically operate at the lower end of OWT zones.

ORP control zones shift slightly more positive as temperature is lowered. Well-operated systems containing sulfite typically reside in the lowest (largest negative number) zones. Weaker reductant use

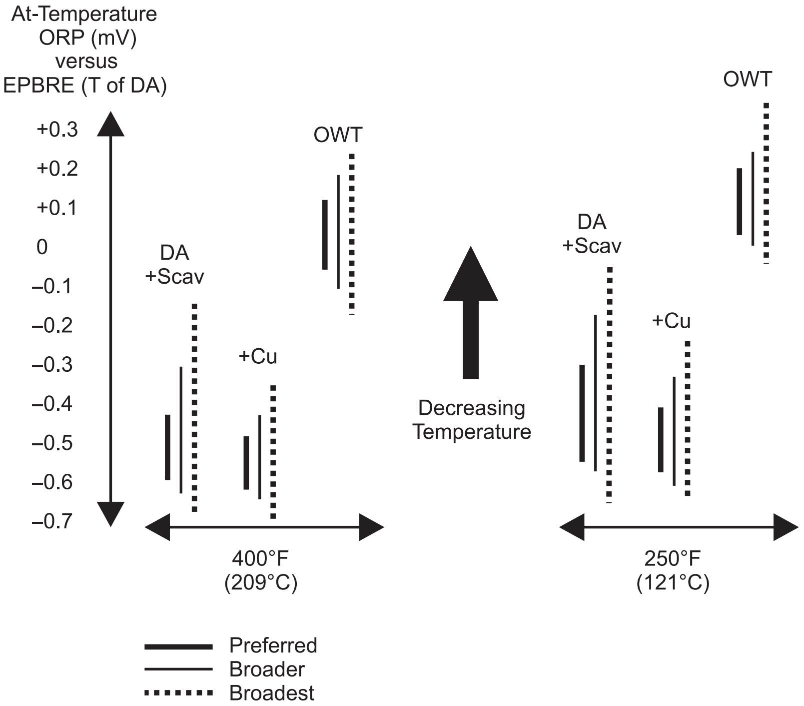


FIGURE 10.20 Examples of ORP control zones in boiler feedwater.

results in higher ORP values. Control zones shift as a function of background dissolved oxygen and pH. Systems tending to have higher background dissolved oxygen values, that tend to be at lower temperatures than systems that operate with conventional pressurized deaerators, operate at higher ORP control zones. The ultimate goal is always real-time system protection using at-temperature ORP in control mode. This leads to plant-specific control zone selection, based on system specifics.

CHAPTER 11

Boiler Feedwater Treatment

The various concepts and practices associated with boiler cycle chemistry will be approached here from a problem and solution standpoint. The boiler cycle is defined as all the contributing components of the system, from the feedwater to the condensate. The pretreatment, deaeration, and treatment chemicals are all used in the cycle to avoid or eliminate problems associated with dissolved or suspended solids and gases in feedwater. These constituents, if left unchecked, may cause considerable damage throughout a steam system.

Table 11.1 illustrates the four major problems associated with boiler systems and where these problems are likely to occur. Chemical treatment must be approached based upon where in the cycle the problems tend to occur. This table is just an approximation and not an absolute. For example, hardness scale is generally not a problem in a high-pressure boiler [1000 psig (6.9 MPag)]; however, if a condenser leak occurs, hardness will be brought back to the boiler through the condensate, and hardness scale will become a significant problem in short order.

Scale on boiler surfaces can lead to serious problems. Even an extremely thin layer of scale is sufficient to retard heat transfer and reduce boiler efficiency. More importantly, scale can cause the boiler heat transfer surfaces to overheat, leading to failures.

The major step in preventing boiler waterside scale is, the careful control and maintenance of all makeup and feedwater pretreatment systems, to limit the amount of impurities entering the boiler. Proper chemical treatment plays a critical role in scale control and is used to inhibit the deposition of minerals that do make their way into the boiler.

This chapter is primarily concerned with industrial boilers. Chapter 33 on the Power Industry contains a discussion of boiler water treatment for high-pressure utility boilers. Some industrial boilers using high-purity feedwater might also use the boiler water

Major Problem	Deaerator	Feedwater System	LP Boiler	HP Boiler	Superheater/ Reheater	Turbine	Steam System	Condensate System
Scale								
Hardness		X	X					
Silica			X	X		X		
Iron	X	X	X	X	X			X
Corrosion								
Oxygen	X	X	X	X	X		X	X
Alkalinity (CO_2)				X		X	X	X
Ammonia		X					X	X
Chelate		X	X					
Deposits								
Metal oxides	X	X	X	X	X			X
Organics		X	X	X				
Carryover								
Entrained liquids			X	X	X	X	X	
TDS*			X	X	X	X	X	

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*TDS = total dissolved solids

Table 11.1 Common Problems and Affected Areas in Boilers treatments discussed in Chap. 33. The boiler owner/operator in conjunction with the water treatment supplier must determine the correct internal treatment program and boiler water operating limits for each application.

Hardness Scale

The primary reason scale forms is that the solubility of the scale forming salts in water decrease as the temperature and concentrations increase. When feedwater is elevated to boiler water temperature, and the concentration of the scale-forming salts exceeds solubility, the salts precipitate, and scale forms (see Table 11.2).

Mineral scale formation (the precipitation of calcium and magnesium salts) usually occurs in boiler feedwater systems (economizers, feedwater pumps, and feedwater lines) and in low-pressure boilers [<1000 psig (6.9 MPag)], where no pretreatment or poorly maintained ion exchange softening is used. Mineral scale is normally not found in boiler systems where demineralization is used or in high-pressure, high-purity systems. The exception to this is where there has been an upset condition such as a condenser leak or a process leak, and the condensate is contaminated with hardness.

	Solubility (g/L as $CaCO_3$)	
Compound	**32°F (0°C)**	**212°F (100°C)**
Calcium		
Bicarbonate	1.6	decomposes
Carbonate	0.015	0.013
Sulfate	1.29	1.25
Magnesium		
Bicarbonate	37.1	decomposes
Carbonate	0.1	0.075
Sulfate	170	356
Sodium		
Bicarbonate	38.7	decomposes
Carbonate	61.4	290
Chloride	225	243
Hydroxide	370	970
Sulfate	33.6	210

TABLE 11.2 Solubility of Chemical Compounds

Scale forms in improperly treated boiler water systems by one or both of the following mechanisms:

1. The precipitation of relatively insoluble feedwater hardness compounds. Calcium carbonate precipitation at the metal surface is one example.

   $$\mathrm{Ca(HCO_3)_2 + heat \rightarrow CaCO_3 + H_2O + CO_2} \quad (11.1)$$

   Uninhibited precipitation tends to form hard scale if it occurs at metal surfaces that are subject to heat transfer.

   Magnesium silicate is found in low-pressure systems where sufficient amounts of magnesium are present in conjunction with adequate amounts of silicate ions and a deficiency of free hydrate alkalinity.

   $$\mathrm{Mg^{+2} + OH^- \rightarrow MgOH^+} \quad (11.2)$$

   $$\mathrm{H_2SiO_3 \rightarrow H^+ + HSiO_3^-} \quad (11.3)$$

   $$\mathrm{MgOH^+ + HSiO_3^- \rightarrow MgSiO_3 + H_2O} \quad (11.4)$$

2. The supersaturation or crystallization of dissolved solids such as calcium sulfate ($CaSO_4$) and silica (SiO_2) in water that contacts heat transfer surfaces. The thin viscous film of boiler water immediately adjacent to the heating surface tends to become more concentrated than the main body of boiler water. As the steam bubbles form, they depart from the metal surface, leaving behind a circular deposit. Eventually, the circular formation is completely filled in with scale. This may occur even though the concentration throughout the main body of the solution does not exceed the solubility limits. Even the most soluble sodium salts may deposit if water is allowed to evaporate to dryness due to plugging, poor circulation, or excessive heat transfer rates.

Scale rarely exists in the pure compound form; it is generally found as complex molecules or as a mixture of compounds within any given sample. Table 11.3 lists the various scales commonly found in feedwater and low-pressure boiler systems.

Silica Scale

Silica-based deposits are found primarily in lower-pressure systems [<1000 psig (6.9 MPag)], where the pretreatment system is not designed for silica removal, that is, sodium softening, or where the

Name	Formula
Acmite	$Na_2O\ Fe_2O_3\ 4SiO_2$
Analcite	$Na_2O\ Al_2O_3\ 4SiO_2\ 2H_2O$
Anhydrite	$CaSO_4$
Aragonite	$CaCO_3$ (gamma form)
Brucite	$Mg(OH)_2$
Calcium hydroxide	$Ca(OH)_2$
Calcite	$CaCO_3$ (beta form)
Copper	Cu
Cuprite	Cu_2O
Ferrous oxide	FeO
Goethite	$Fe_2O_3\ H_2O$ (alpha form)
Gypsum	$CaSO_4\ 2H_2O$
Hematite	Fe_2O_3
Hydroxyapatite	$Ca_{10}(PO_4)_6(OH)_2$
Lizardite (formerly serpentine)	$3MgO\ 2SiO_2\ 2H_2O$
Magnesium hydroxy phosphate	$Mg_3(PO_4)_2\ Mg(OH)_2$
Magnetite	Fe_3O_4
Sodium ferrous phosphate	$NaFePO_4$
Tenorite	CuO
Thenardite	Na_2SO_4
Xonotlite	$5CaO\ 5SiO_2\ H_2O$

Table 11.3 Common Constituents Found in Boiler Deposits

boiler is operated at excessive cycles of concentration. Although uncommon, silica-based deposits can be found in high-pressure systems, where silica leakage through the anion unit(s) has been a problem. Silica-based deposits become more serious as silica increases and hydrate alkalinity decreases.

Silica can form several types of deposits, such as amorphous silica and magnesium silicate. Amorphous silica appears as a smooth glass-like deposit that is very difficult to remove and is generally cleaned with a hydrofluoric acid solvent. Magnesium silicate generally is tan to off-white and has a somewhat rough texture. Although magnesium silicate is easier to remove than amorphous silica, it is still difficult. Both forms of silica have high insulating properties and can result in tube failures in watertube boilers.

Silica, in addition to forming boiler deposits, can vaporize from the boiler and be carried with the saturated steam as silicic acid.

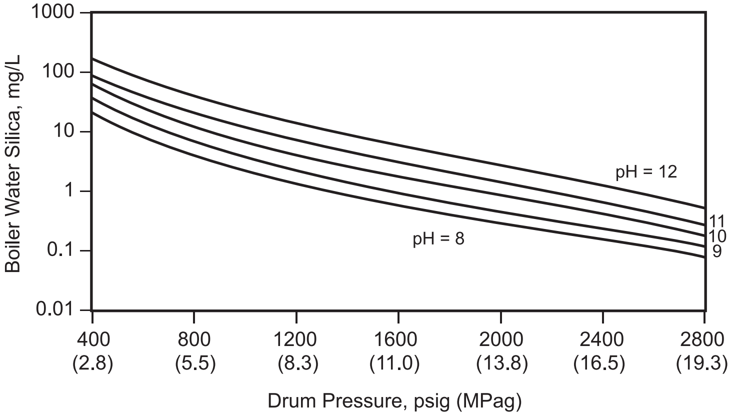

Figure 11.1 Effect of drum pressure and pH on allowable silica concentration to maintain steam purity target of 20 μg/L.

When the steam containing vaporous silica performs work and has some of the superheat content reduced such as going through a turbine, the silica precipitates on the metal surfaces causing deposits. This deposit will reduce the efficiency of the turbine and can result in an imbalance of the turbine wheels. Additionally, unlike sodium-based deposits that can be removed with water washing, the silica deposits are very difficult to remove. Selective silica carryover is not a serious problem below 600 psig (4.1 MPag); however, it can become a very serious problem as the pressure increases, particularly above a pressure of 1000 psig (6.9 MPag).

Figure 11.1 shows the relationship of boiler pressure to the maximum permissible concentration of silica in the boiler water in order to maintain less than 20 μg/L of silica in the steam (the typical maximum concentration allowed in the steam supplying steam turbines).

Silica control is very important; it can be achieved through proper pretreatment and proper boiler blowdown. In low-pressure boilers using a phosphate-polymer internal treatment program, silica deposition in the boiler can be controlled by maintaining at least a 3:1 ratio of hydrate alkalinity to silica.

Iron Deposits

Iron oxides present in boiler water have caused problems since the dawn of boilers. However, in the beginning, iron deposits were not the major problem or root cause of most boiler failures, as were hardness scale deposits. As the design of boilers evolved from low-pressure, riveted, drum-type boilers, to today's modern high-pressure, high heat flux, thin-walled watertube boilers, the requirement for higher purity boiler feedwater also occurred. The effective removal of calcium and magnesium from boiler feedwater by pretreatment techniques such as lime softening, sodium softening, ion exchange demineralization, and reverse osmosis (RO) has shifted the cause for boiler failures to be predominately due to iron deposits on the heat transfer surface. These deposits cause under-deposit corrosion problems and act as insulators, impairing heat transfer, which can cause the boiler metal to overheat and ultimately fail.

The energy crisis in the early 1970s, caused by the Organization of Oil Exporting Countries (OPEC) oil embargo, had a major impact on industry and the boiler iron story. The loss of cheap energy, and the need to conserve energy, led industry to focus on returning more and more steam condensate as a source of boiler feedwater, due to its valuable energy content and relative high purity. However, the consequence of increasing the amount of returned condensate to the boiler, was the increased amount of iron oxide corrosion products entering the boiler. Most of the corrosion products that deposit in the boiler originate in the steam condensate system. Corrosion of the feedwater piping, economizer, and boiler, as well as the iron entering with the makeup water, are other sources contributing to the boiler iron deposit problem.

The Problem with Iron

Both soluble and insoluble iron (particulate and colloidal) can be present in boiler feedwater and boiler water. Boiler water iron will deposit on the steam generating surfaces of the boiler and cause under-deposit corrosion and overheating problems. Iron deposits on the heat transfer surfaces are typically hard, dense, and porous. The porosity of the deposits allow wick boiling to occur, which provides a mechanism for concentrating and trapping corrosive chemistries such as caustic, acid phosphates, sulfates, and chlorides inside the deposit. In addition, the insulating property of the deposit impairs heat transfer and causes the temperature of the boiler metal to increase.

As shown in Table 11.4, iron oxide deposits are insulating, with hematite deposits being more insulating than magnetite. Note that the values in Table 11.4 do not incorporate the effect of deposit porosity, which varies and affects the actual thermal conductivity. To prevent overheating and rupture of boiler tubes due to the continued buildup of iron deposits, boilers must be acid cleaned periodically.

Iron Deposition Mechanism

Steam generation in boilers generally occurs under nucleate boiling conditions, where discrete steam bubbles form and break away from the surface, allowing fresh boiler water to reach the surface to cool and clean it and start the process again. Soluble and suspended materials concentrate at the vapor/liquid interface of the bubble

Compound	**Thermal Conductivity**	
	Btu/[h·ft·°F]	**W/[m·K]**
Calcium phosphate	2.1	3.6
Magnetite	1.7	2.9
Magnesium phosphate	1.2	2.1
Calcium sulfate	0.75	1.3
Lizardite (serpentine)	0.58	1.0
Calcium carbonate	0.53	0.92
Hematite	0.34	0.59
Carbon steel	26.7	46

TABLE 11.4 Thermal Conductivity of Typical Boiler Deposits

(meniscus of the steam bubble) as well as at the point of bubble attachment to the boiler tube. Figure 11.2 is a simple illustration of the growth cycle of a single steam bubble. Deposits occur at the wet/dry interface on the tube surface. The amount of deposit is equal to, or slightly more than, what was contained in the liquid that was vaporized to steam. As the bubble breaks away, fresh liquid sweeps the surface, removing all or some of the solid. Any deposit left behind is eventually baked onto the surface.

Conceptually, Fig. 11.2 is easy to understand. However, the deposition process is far more complicated. A collaborative research project conducted in the mid-1990s by Nalco and Argonne National Laboratory studied the mechanism of iron deposition under nucleate boiling conditions. Factors affecting deposition of iron were found to include pressure, temperature, heat flux, iron concentration, pH, surface roughness (macro and micro), time of bubble attachment, flow rate, and other impurities present in the water.

The research showed that hematite particles tended to agglomerate during the formation, growth, and release of the steam bubble. Interestingly, it was found that the amount of iron deposited on the surface was sixty times more than what is predicted from the simple evaporation to dryness deposition model shown in Fig. 11.2. This finding suggests that there is a complex particle-bubble interaction. It is hypothesized that since the steam vapor inside the bubble is less polar (more hydrophobic) than the boiler water, this causes the hematite particles in the surrounding boiler water adjacent to the bubble to migrate toward and concentrate in the steam bubble meniscus. Then, through capillary and eddy current effects, the iron is drawn down to the surface and deposited at the bubble attachment point.

Heat flux and iron concentration have a significant effect on the deposition rate. The higher the heat flux, the more iron is deposited

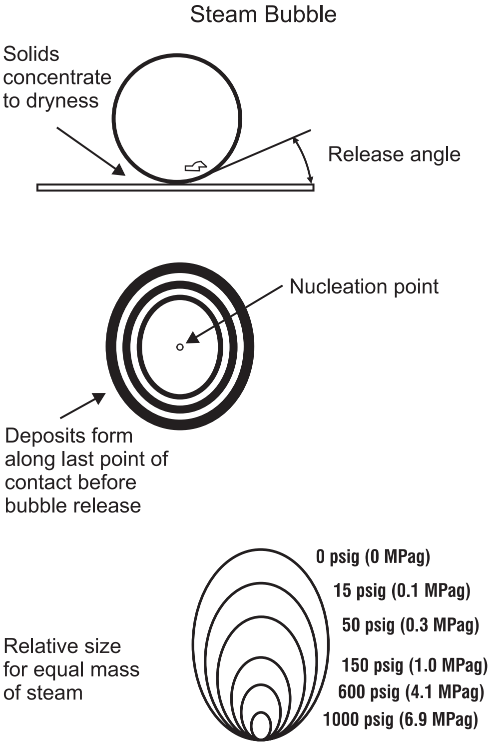

FIGURE 11.2 Steam bubble formation.

per unit time. The rate of iron oxide deposition was found to follow first-order kinetics with respect to iron in the boiler water.

Sources of Iron

Iron entering the boiler originates from two main sources:

1. Naturally occurring iron present in the raw water
2. Corrosion of the mild steel components making up the boiler system, including preboiler and post-boiler

Raw water can contain soluble iron salts and particulate/colloidal iron hydroxides and oxides. For instance, well water can contain high levels of soluble iron, which is oxidized to convert the iron to insoluble oxides and hydroxides, to enhance removal during the pretreatment process. In the case of surface water, iron is predominantly present as insoluble iron oxides and hydroxides, because the dissolved oxygen level in the water is sufficient to oxidize the iron and cause its precipitation.

Corrosion of the mild steel components in the pretreatment, feedwater, boiler, and condensate systems is the major source of iron entering the boiler. There are a number of corrosion mechanisms.[1]

Factors affecting mild steel corrosion in boiler systems include pH, temperature, heat flux, dissolved oxygen, carbon dioxide, flow, ionic strength, suspended solids, and boiler treatment chemicals such as chelants and polymers.

Mild steel is used in the construction of boiler systems because of its mechanical strength, high thermal conductivity, and low cost. In addition, mild steel at high temperature under alkaline reducing conditions forms a protective thin adherent magnetite oxide (Fe_3O_4) layer on the surface, which is self-limiting and protects the base metal from the corrosive aqueous environment. Therefore, the recommended pH range for boiler water is 9 to 12 (Fig. 11.3).

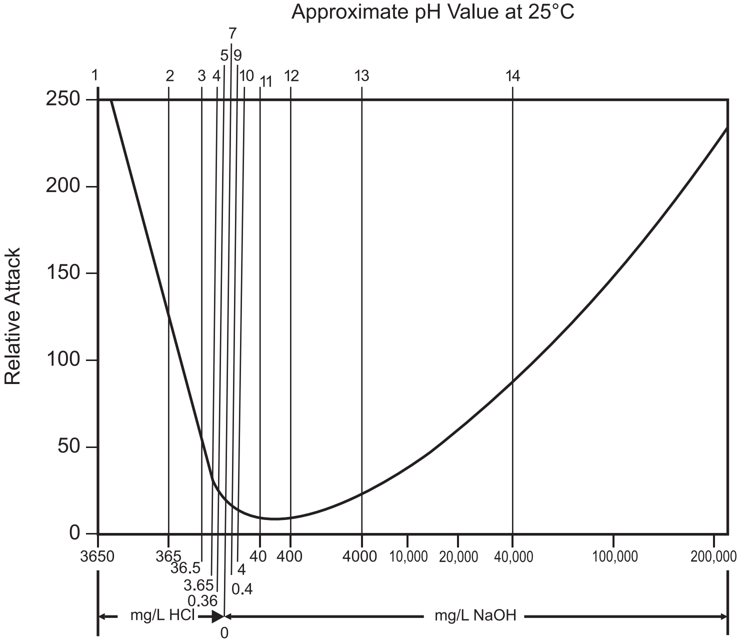

Figure 11.3 Relative corrosion rate of boiler steel versus pH and caustic concentration.

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[1] For a more in-depth coverage of corrosion failures in boilers, refer to Dillon, J.J., Desch, P.B., Lai. T.S., Flynn, D.J., ed, *The NALCO Guide to Boiler Failure Analysis*, 2nd ed. McGraw-Hill, New York, NY, 2011.

The mechanism of magnetite formation, the Schikorr reaction, proceeds through the following steps:

$$Fe + 2H_2O \rightarrow Fe^{+2} + 2OH^- + H_2 \tag{11.5}$$

$$Fe^{+2} + 2OH \rightleftharpoons Fe(OH)_2 \tag{11.6}$$

$$3Fe(OH)_2 \rightarrow Fe_3O_4 + 2H_2O + H_2 \tag{11.7}$$

The formation of ferrous hydroxide [Eq. (11.6)] is the rate-limiting step to the overall production of magnetite, and it is slow below 400°F (204°C). The controlled corrosion process of passivation is achieved as the metal surface goes from an actively corroding state [Eq. (11.5)] to an inactive steady state [Eq. (11.7)]. Since hydrogen is released as the metal becomes passive, hydrogen evolution accompanies the formation of the magnetite film. It has been widely recognized that monitoring hydrogen in the steam of a boiler is an indirect measure of the boiler corrosion activity.

In addition, it should be noted that ferrous ions (Fe^{+2}) are the first product of corrosion [Eq. (11.5)]. Measuring the concentration of Fe^{+2} is an important method to identify active corrosion in boiler systems. Quantifying Fe^{+2} is an important part of the iron control prevention strategy. Any condition leading to the damage of the magnetite protective oxide film will cause an increase in corrosion of the base metal. Mechanical and thermal stresses can fracture the oxide layer creating microcracks, which expose the base metal and allow the corrosion reactions to proceed.

These stresses can eventually lead to exfoliation of portions of the oxide layer, which again exposes the base metal to further corrosion and allows the potential migration of particulate iron to reach the boiler and deposit on the steam generating surfaces. For example, when a paper machine comes back online after being down because of a paper break or some other reason, high levels of suspended iron are initially found in the return condensate. The longer the paper machine is off-line, the worse the situation (high iron content for longer period of time in the condensate). The reason for the iron throw is that the mild steel components went through a contraction and expansion cycle during the shutdown/startup period, causing the oxides to fracture and exfoliate because they are less ductile than mild steel. Additionally, as the system cools down, air is drawn in, and oxygen corrosion attack occurs.

Chemical attack leading to dissolution of the magnetite protective layer will increase the corrosion of mild steel. For instance, high concentrations of caustic or acid can lead to severe corrosion problems in boilers. In addition, chemical species, which interact or complex with the ferrous ion such as chelants, chlorides, sulfates, polymers, and hydroxyl ions, may prevent the formation of magnetite by limiting Eqs. (11.6) and (11.7). The net result of this effect could be an increase in corrosion due to an increase in the rate of metal dissolution.

Polymers and Iron Control

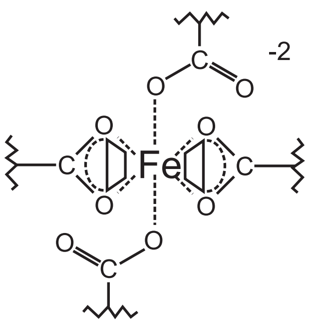
Polymers do play an important role in the iron control strategy; they are the last line of defense. Polymers have the ability to inhibit agglomeration of iron particles, keeping them dispersed in the boiler water, and to reduce the rate of iron oxide deposition on the heat transfer surfaces. The two types of polymers Nalco uses are polymethacrylate and copolymers of acrylate/styrene sulfonate (NexGuard®). These anionic polymers absorb onto the negatively charged iron particles and prevent the particles from agglomerating through charge-charge repulsion and by steric hindrance.

Molecular weight and pH can affect the dispersant properties of anionic polymers. In general, as the pH goes up, the dispersant activity does too. Lower molecular weight anionic polymers are more effective than high molecular weight anionic polymers.

In addition to their dispersant properties, anionic polymers are known to complex iron and solubilize iron in a similar fashion as chelants, although their complexing strength is less than that of chelants. Figure 11.4 illustrates how polymers complex iron.

Consequently, polymers can cause feedwater and boiler water corrosion problems. It is important to monitor the generation of soluble iron (Fe^{+2}) and total iron (Fe^{+2} + Fe^{+3}) in the feedwater and blowdown when feeding polymers to determine the optimum product dosage. Total iron testing alone in the feedwater and blowdown cannot differentiate between iron oxide particulate and active corrosion. Figure 11.5 shows the relationship between soluble iron and total iron in boiler blowdown.

As the dosage of the polymer treatment increases, the concentration of particulate iron (Fe^{+3}) increases in the blowdown, then plateaus and remains constant regardless of further increases in dispersant



Multiple polymer chains interact with metal ion

Several carboxyl groups of the same polymer chain may be involved

Not STATIC! Free movement of metal ion along polymer chain

Figure 11.4 Polymer complexing iron.

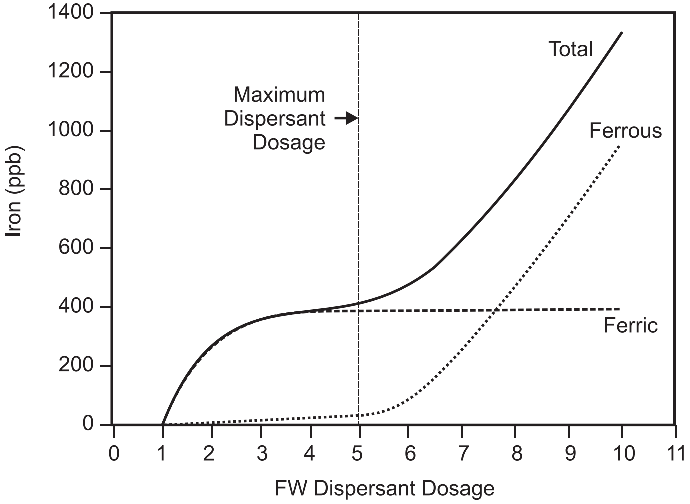


Figure 11.5 Soluble versus total iron in boiler blowdown.

dosage. The initial increase represented the improvement in iron oxide particle dispersion caused by the polymer. As the polymer dosage increases further, ferrous iron (Fe^{+2}) concentration begins to rise in the blowdown, until a near linear relationship between increased dosage and increased Fe^{+2} is established. The data show that increasing the polymer dosage above a certain level does not increase the dispersion of iron oxide particles and their removal, but only leads to increased corrosion.

A good rule of thumb is that the boiler water Fe^{+2} concentration should never be greater than the feedwater Fe^{+2} concentration times cycles, and feedwater Fe^{+2} should be low (2–5 μg/L) in a well-protected system.

Molecular weight, flow, temperature, pH, and polymer concentration affect the corrosivity of anionic polymers toward mild steel. Low molecular weight anionic polymers were found to be more corrosive than high molecular weight polymers. Designing an effective and noncorrosive polymeric iron dispersant for boiler applications requires optimizing chemical structure and molecular weight.

Iron Control

Effective iron control can be summed up in three words: prevention, prevention, and prevention. The best control strategy is to prevent iron from entering the boiler, because iron deposits in the boiler can lead to:

- Under-deposit corrosion problems
- Overheating problems resulting in boiler tube failures

- Unscheduled outages that result in lost production and lost profits
- Higher frequency of boiler acid cleanings
- Increase in capital expenditures

However, since the late 1970s, with the introduction of synthetic polymeric dispersants, the term boiler iron control has come to mean feeding polymeric boiler iron dispersants. In general, focus has been lost on prevention, and the single prong approach or philosophy that one can cure the iron problem by feeding polymer to the boiler and transporting the iron through the boiler has been adopted.

Over the past 20 years, we have learned a lot about iron deposition and control in boilers through extensive laboratory research, field trials, collaborative research studies with Argonne National Laboratory, and published literature from the Electric Power Research Institute (EPRI) and others. Iron transport studies conducted in the field and in our laboratory's experimental boilers indicate that the majority of iron entering the boiler remains in the boiler, even when dispersants are used.

A major reason for the poor transport results is that boilers are not designed to remove suspended materials effectively. The boiler continuous blowdown line is designed to remove soluble species efficiently and is not optimized to remove particulate matter. Surface blowdown will remove some particulate, but it is not isokinetically designed to remove two-phase material (liquid and solids). This is why intermittent manual blowdown of the mud drum is practiced. Another reason for poor transport is that much of the iron reaching the steam generating surfaces of the boiler will deposit and will not be available for removal by blowdown.

However, research work has shown that polymers do affect the rate of iron deposition on the heat transfer surfaces of boilers and, thus, are an important aspect of overall boiler iron control. Polymers can slowdown the rate of iron deposition and help keep the heat transfer surfaces cleaner longer.

Although polymers slow the deposition rate, iron oxide deposition rate follows first-order kinetics with respect to iron concentration. In addition, the higher the heat flux, the faster the rate of deposition. These two findings, coupled with the fact that most of the iron is not transported through the boiler, means that the primary method to control iron deposits in boilers is to prevent iron from entering the boiler in the first place. This statement is strongly supported by the cycle chemistry guidelines published by the American Society of Mechanical Engineers (ASME), EPRI, VGB (a German organization of large power station operators), Japanese Boiler Manufacturers, and the British Boiler Standards. These guidelines stress the importance of keeping the feedwater iron concentration very low (μg/L levels).

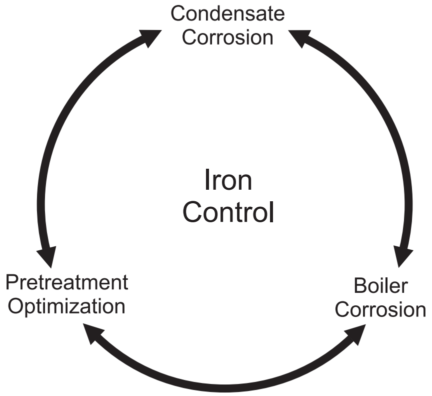


Figure 11.6 Iron control triangle.

As a result of this collective knowledge, the preferred iron control strategy today concentrates on the iron control triangle offense of prevention as shown in Fig. 11.6.

First, prevent iron contribution from the makeup water by optimizing pretreatment iron removal. Secondly, minimize iron returned via the steam condensate system by inhibiting condensate corrosion and maximizing the removal of any iron present in the returned condensate through use of condensate polishers/filters and automatic dump systems. The third leg of the triangle offense is to minimize corrosion from boiler feedwater and boiler water.

To be successful, the triangle control strategy requires implementing the mechanical, operational, and chemical (MOC) approach, not just a chemical treatment approach. For instance, it is critical to do iron profiling of the makeup water pretreatment system, the condensate system, at the deaerator, at the inlet and outlet of the economizer, and the boiler blowdown. It is necessary to determine where the iron is coming from, how much iron is there, and to determine the form of the iron, in order to identify if the iron is a result of active corrosion (soluble Fe^{+2}) or migration of old iron oxide corrosion products (insoluble particulate Fe^{+3}). Determining the iron removal efficiency and optimizing the performance of plant equipment such as condensate polishers, ion exchange units, carbon or sand filters, and magnetic filters, is very important. Determining if these units are backwashed properly and rinsed down long enough prior to returning the units back into service mode is important because, if done improperly, it may lead to slugs of particulate iron reaching the boiler.

The chemical iron prevention technologies available in the triangle control strategy are:

- Caustic
- Phosphate products

- Organic and inorganic oxygen scavengers
- Condensate neutralizing amines
- Filming amines
- Nonamine filmer (Nalco ACT®)
- Ion exchange resin cleaners (for iron and organic foulant removal)

In the triangle control strategy, iron dispersants are considered defensive chemistries, because they do not prevent iron from entering the boiler.

Preventing iron from entering the boiler is, by far, the best approach to eliminating boiler tube failures caused by iron deposits. Feeding small doses of polymeric iron dispersants (substoichiometric to iron) is warranted, because they can slowdown the iron deposition rate. It is also recommended that boilers not operate at excessively high cycles, because the deposition rate is dependent on the iron concentration. Operating with at least 2% blowdown (50 cycles) in industrial boilers and 1% blowdown (100 cycles) in electric utility boilers is generally effective for good iron control.

Effects of Boiler Scale

Boiler scale creates a problem in boiler operation because all the different types of scale possess a low thermal conductivity. The presence of scale is equivalent to having a thin film of insulation across the path of heat travel from the furnace gases to the boiler water. This heat-insulating material retards heat transfer and can cause a loss in boiler efficiency. Stack gas temperatures may increase as the boiler absorbs less heat from the furnace gases. This is more commonly seen in firetube boilers, where convective heat transfer is more dominant. This is usually not seen in watertube boilers, where radiant heat transfer is the primary mechanism.

The chemical structure of the scale, its porosity, and its thickness, as well as the design and method of operation of the boiler, all influence the amount of heat lost. Heat transfer may be reduced as much as 10 to 12% by the presence of scale. A scale approximately 1/8 inch (3 mm) thick may cause an overall loss in boiler efficiency of 2 to 3% in firetube boilers. In watertube boilers, the presence of scale is more a problem in boiler reliability than efficiency loss.

Even more important than the heat loss is that scale causes overheating of the boiler tube metal and can result in subsequent tube failures. Costly repairs and boiler outages are the results of such a condition. In modern boilers with high heat transfer rates in excess of 150 000 Btu/[h · ft^2] (473 kW/m^2), even extremely thin layers of scale will cause a serious elevation in the temperature of

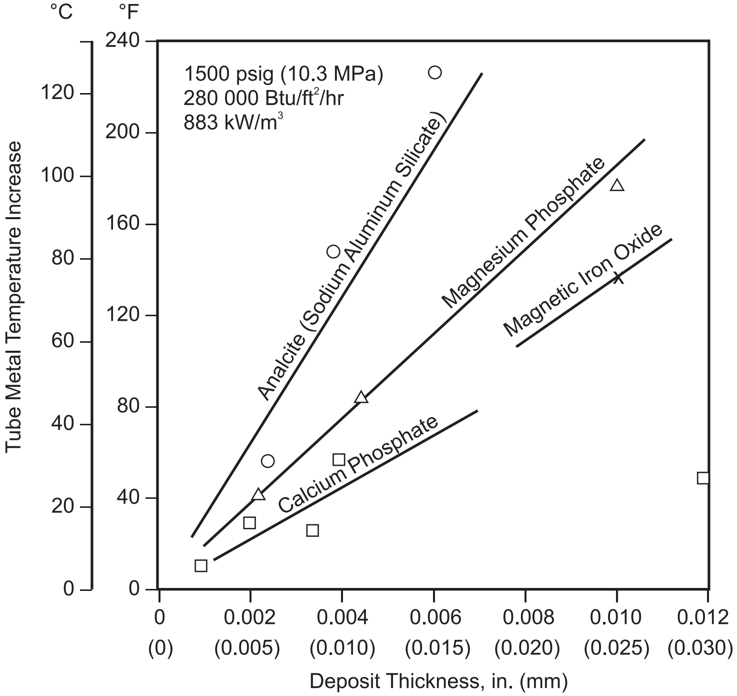


Figure 11.7 Effects of boiler scale on tube metal temperature.

tube metal (Fig. 11.7). The scale coating retards the flow of heat from the furnace gases into the boiler water. This heat resistance results in a rise in metal temperature to the point at which failure can occur.

Figure 11.8 illustrates the action that takes place in the blistering of a tube because of scale formation. For simplification, temperature drops through gas or water films have not been shown. Section A shows a cross section of the tube metal with a completely scale-free heating surface. There is a temperature drop across the tube metal from the outside metal temperature T_2 to the temperature of the boiler water T_1. Section B illustrates this same tube after a heat-insulating scale layer has formed. In addition to the temperature drop from T_2 to T_1, there would be an additional temperature drop through the scale layer from T_1 to T_0. This condition, of course, would result in a lower boiler water temperature (T_0). However, boiler water temperature is fixed by the operating pressure, and operating conditions require that the same boiler water temperature T_1 be maintained as before the development of the scale layer. Thus, the tube outside metal temperature will be elevated to maintain the same steam generation at the specified temperature and pressure.

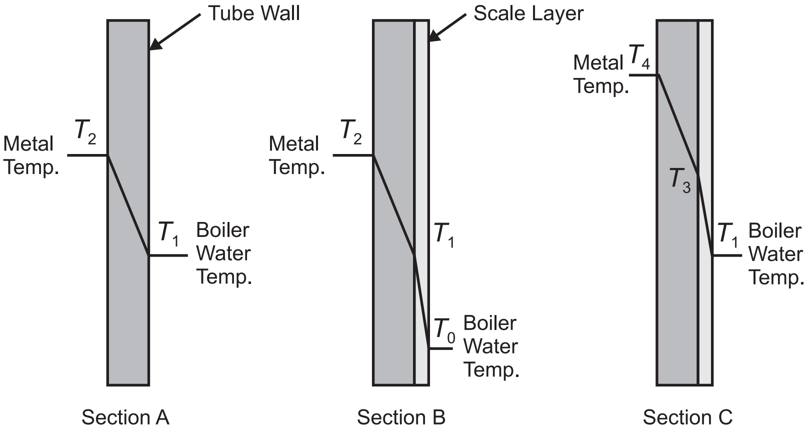


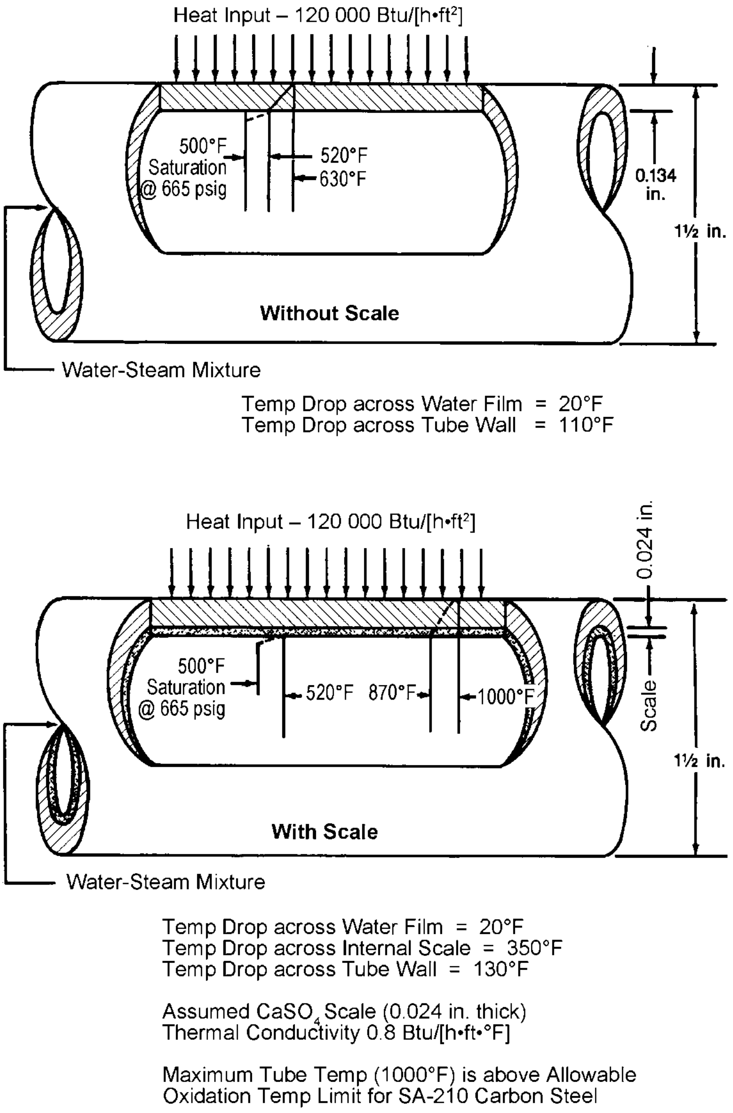
Figure 11.8 Effect of scale on boiler heating surfaces.

Section C illustrates the condition that actually develops. Starting at the base boiler water temperature of T_1, the temperature increase through the scale layer is represented by the line from T_1 to T_3. The further temperature increase through the tube wall is represented by the line from T_3 to T_4. The outside metal temperature T_4 is now considerably higher than the temperature T_2, which was the outside metal temperature before the formation of scale on the tube surface.

If scale deposition continues, increasing the thickness of the heat-insulating deposits, tube metal temperature will continue to increase until the safe maximum temperature [usually 900°F (482°C) for the typical carbon steel tube] is exceeded.

Figures 11.9 and 11.10 show the effect of a 0.024 inch (0.61 mm) layer of calcium sulfate scale on a moderately high heat flux boiler tube. The effects of the water/steam film on the inside wall of the tube are shown to further illustrate how only a small amount of scale can quickly result in tube failure. With higher boiler pressures [>1000 psig (6.9 MPag)] and, therefore higher boiler water temperatures, there is less of a temperature difference between the boiler water saturation temperature and the metal. Consequently, in high-pressure systems, even very thin layers of scale can cause failures.

Additionally, in boilers with high heat transfer rates, scale deposition can promote localized under-deposit corrosion. This secondary corrosion effect is particularly evident in systems that have iron oxide deposition, which are porous deposits. Boiler water can seep through these deposits to the boiler metal, where it will evaporate to steam, leaving behind the dissolved solids. Dissolved solids in the boiler



Temp Drop across Water Film = 20°F
Temp Drop across Tube Wall = 110°F

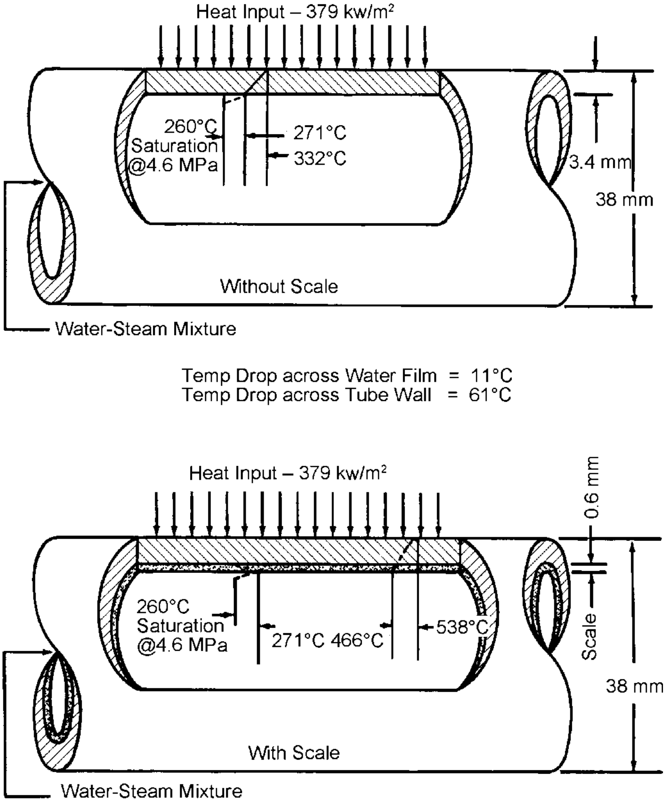
Temp Drop across Water Film = 20°F
Temp Drop across Internal Scale = 350°F
Temp Drop across Tube Wall = 130°F

Assumed $CaSO_4$ Scale (0.024 in. thick)
Thermal Conductivity 0.8 Btu/[h•ft•°F]

Maximum Tube Temp (1000°F) is above Allowable
Oxidation Temp Limit for SA-210 Carbon Steel

Figure 11.9 Effect of calcium sulfate scale on high heat flux boiler tube—U.S. units.

water such as caustic and chloride can concentrate in these localized areas to thousands of milligrams per liter, even though the bulk water contains normal recommended levels of these species. These high concentrations can result in rapid and severe metal dissolution and failure.



Temp Drop across Water Film = 11°C
Temp Drop across Tube Wall = 61°C

Temp Drop across Water Film = 11°C
Temp Drop across Internal Scale = 195°C
Temp Drop across Tube Wall = 72°C

Assumed $CaSO_4$ Scale 0.61 mm
Thermal Conductivity 1.44 W/[m•K]

Maximum Tube Temp (538°C) is above Allowable
Oxidation Temp Limit for SA-210 Carbon Steel

Figure 11.10 Effect of calcium sulfate scale on high heat flux boiler tube—metric units.

Internal Chemical Treatment Programs

Scale formation in low-pressure boilers [<1000 psig (6.9 MPag)] and feedwater systems can be controlled in two primary ways:

1. Proper operation and maintenance of all makeup and feedwater pretreatment systems. Hot and cold lime softeners, filters, sodium softeners, water-cooled packing glands on feedwater pumps, etc., must be operating properly before chemical treatment can be effectively applied. Otherwise,

erratic and unpredictable quantities of scale-forming components will be fed to the boiler system, and results will be compromised.

2. Chemical treatment is then used to condition any remaining minerals leaking through to the boiler. Among the treatments in common use today are:
    - Coagulation treatment programs that were commonly used in the past (1900–1950). Although still in use today, modern, inexpensive pretreatment technology has made their use almost obsolete
    - Phosphates (residual with and without polymer)
    - Chelates
    - All-polymer treatments

Phosphate Residual Programs—Low Pressure Industrial Systems

Tricalcium phosphate has an extremely low solubility. Hence, when properly controlled, the addition of phosphate to boiler water removes calcium so completely and efficiently that calcium sulfate, calcium carbonate, and calcium silicate scales can be prevented. In the presence of sufficient alkalinity, the actual phosphate precipitate formed is calcium hydroxyapatite $[Ca_{10}(PO_4)_6(OH)_2]$, which is a less sticky, more readily conditioned reaction product than tricalcium phosphate.

Although phosphate can precipitate with magnesium as magnesium phosphate if the phosphate is overfed, proper boiler chemistry will preferentially precipitate magnesium as a less adherent and more easily conditioned magnesium hydroxide, magnesium silicate, or the preferred lizardite $Mg_3Si_2O_5(OH)_4$ (formerly serpentine). The best solution to boiler scale is proper softening of the makeup water to remove all calcium and magnesium, followed by a good chemical control program.

Phosphate residual programs are acceptable where feedwater hardness is less than 0.3 mg/L.[2] Numerous chemicals can be used to furnish the phosphate ion necessary for internal softening treatment. Compounds of the orthophosphate ion (PO_4^{-3}) are the most widely used. Other phosphate ions that can be used are meta (PO_3^-), tripoly ($P_3O_{10}^{-5}$), and pyro ($P_2O_7^{-4}$). Some of these salts are called polyphosphates because they form inorganic polymers. Among these are the glassy sodium polyphosphates (hexa- and heptametaphosphate) and crystalline sodium polyphosphates such as sodium tripolyphosphate

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[2] Consensus on Operating Practices for the Control of Feedwater and Boiler Water Chemistry in Modern Industrial Boilers, ASME, 1994.

and tetrasodium pyrophosphate. The polyphosphates can be described as molecularly dehydrated orthophosphates. When added to water, polyphosphates rehydrate (at a rate that is temperature dependent) to the orthophosphate form from which they were derived.

Although this discussion of phosphates is rather limited, it is a reminder that the precipitation of tricalcium phosphate (or calcium hydroxyapatite) in the boiler can occur only when the phosphate in use has been converted to trisodium orthophosphate by heat and reacted with boiler alkalinity.

If the product is to be fed directly to the steam drum of a boiler, the best choice is an orthophosphate formulation, because the conversion to trisodium orthophosphate (in the case of mono- or disodium orthophosphate) is extremely rapid. Conversely, feeding a meta- or pyrophosphate (polyphosphate) directly to the boiler may delay chemical reactions undesirably. This is particularly true if the boiler pressure is less than 50 psig (345 kPag) and if the cycles of concentration are low (<10). If a phosphate product is fed directly to a boiler steam drum or feedwater, where water temperature exceeds 400°F (204°C), the product should be diluted to less than a 10% solution of the product, or feed the undiluted (neat) product into a feedwater bypass line into the drum. The feed of a concentrated product directly into the steam drum, or feedwater line of greater than 400°F (204°C), may result in plugging the chemical feed line. If, on the other hand, a phosphate is to be fed to the boiler feedwater, a polyphosphate product is chosen to avoid the possibility of deposits caused by softening reactions occurring in the feedwater lines, economizer tubes, etc. An orthophosphate formulation would be entirely unsuitable for such a feed point. When feedwater hardness is greater than 3 mg/L, all phosphates are usually fed to the steam drum to prevent deposition in the feedwater system and the economizer.

Each of the common phosphates has an effect on boiler water alkalinity as well. When hardness in the feedwater is precipitated by direct reaction with alkalinity (as in a coagulation program), available alkalinity generally decreases.

$$\mathrm{Ca(HCO_3)_2 + heat \rightarrow CaCO_3 + H_2O + CO_2} \tag{11.8}$$

$$\mathrm{CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 + Na_2SO_4} \tag{11.9}$$

$$\mathrm{Mg(HCO_3)_2 + 4NaOH \rightarrow Mg(OH)_2 + 2Na_2CO_3 + 2H_2O} \tag{11.10}$$

$$\mathrm{MgCl_2 + 2NaOH \rightarrow Mg(OH)_2 + 2NaCl} \tag{11.11}$$

When phosphates are used to precipitate the calcium hardness, however, some of the alkalinity associated with calcium hardness is retained in the form of sodium alkalinity in the boiler. The amount of alkalinity retained depends upon the type of phosphate used. Because phosphates must be converted to trisodium orthophosphate in the boiler before precipitation of calcium occurs, some alkalinity consumption results.

$$\underset{\text{(meta)}}{NaPO_3} + 2NaOH \rightarrow \underset{\text{(trisodium)}}{Na_3PO_4} + H_2O \tag{11.12}$$

$$\underset{\text{(pyro)}}{Na_4P_2O_7} + 2NaOH \rightarrow \underset{\text{(trisodium)}}{2Na_3PO_4} + H_2O \tag{11.13}$$

$$\underset{\text{(tripoly)}}{Na_5P_3O_{10}} + 4NaOH \rightarrow \underset{\text{(trisodium)}}{3Na_3PO_4} + 2H_2O \tag{11.14}$$

$$\underset{\text{(disodium)}}{Na_2HPO_4} + NaOH \rightarrow \underset{\text{(trisodium)}}{Na_3PO_4} + H_2O \tag{11.15}$$

$$\underset{\text{(monosodium)}}{NaH_2PO_4} + 2NaOH \rightarrow \underset{\text{(trisodium)}}{Na_3PO_4} + 2H_2O \tag{11.16}$$

Once the phosphate has been converted to trisodium orthophosphate, the reactions with calcium hardness proceed, as shown in Eqs. (11.17) and (11.18). Calcium hardness is represented by $CaSO_4$ and $CaCO_3$, although other species may coexist.

$$2Na_3PO_4 + 3CaCO_3 \rightarrow Ca_3(PO_4)_2 + 3Na_2CO_3 \tag{11.17}$$

$$2Na_3PO_4 + 3CaSO_4 \rightarrow Ca_3(PO_4)_2 + 3Na_2SO_4 \tag{11.18}$$

While the overall tendency when using phosphates to soften the water will be to increase the amount of retained alkalinity in the boiler (as compared to coagulation program reactions), the amount of increase is a function of the type of phosphate used. Thus far, only the amount of phosphate consumed in reacting with calcium has been considered. Because a certain level of phosphate residual is always carried (present as trisodium orthophosphate), additional alkalinity is consumed for each mg/L of phosphate residual required [Eqs. (11.12)–(11.16)]. Hence, the net gain in available alkalinity becomes a function of the following:

- Type of phosphate used
- Amount and form of calcium hardness
- Level of magnesium hardness
- Level of residual phosphate carried

These principles can be demonstrated more clearly if the typical calcium-phosphate reactions are considered as one step, rather than as two separate steps. Equations (11.19) to (11.23) demonstrate the effect on retained sodium alkalinity. The reactions controlling magnesium precipitation [Eqs. (11.10) and (11.11)] and those controlling phosphate conversion for phosphate residuals [Eqs. (11.12)–(11.16)] must be added to these reactions.

$$2Na_3PO_4 + 3CaCO_3 \rightarrow Ca_3(PO_4)_2 + 3Na_2CO_3 \tag{11.19}$$

(trisodium)

$$2Na_2HPO_4 + 3CaCO_3 \rightarrow Ca_3(PO_4)_2 + CO_2 + 2Na_2CO_3 + H_2O \tag{11.20}$$

(disodium)

$$2NaH_2PO_4 + 3CaCO_3 \rightarrow Ca_3(PO_4)_2 + Na_2CO_3 + 2CO_2 + 2H_2O \tag{11.21}$$

(monosodium)

$$2Na_5P_3O_{10} + 9CaCO_3 + 2NaOH \rightarrow 3Ca_3(PO_4)_2 + 6Na_2CO_3 + 3CO_2 + H_2O \tag{11.22}$$

(tripoly)

$$2Na_2HPO_4 + 3CaSO_4 + 2NaOH \rightarrow Ca_3(PO_4)_2 + 3Na_2SO_4 + 2H_2O \tag{11.23}$$

(disodium)

Although these reactions are complex, they are important to understanding boiler water chemistry.

Applications

Phosphate residual treatment programs are best suited for feedwaters that are consistently below 0.30 mg/L hardness, have low magnesium, and have silica content greater than one-third the magnesium content. The greater the feedwater hardness is above 0.3 mg/L the greater the deposit accumulation rate will be in the boiler and the greater the need to periodically clean the boiler as well.

Phosphate programs can be effectively applied to boilers with operating pressures up to 2800 psig (19.3 MPag), although residual phosphate is rarely applied at operating pressures above 1200 psig (8.3 MPag).

Program Controls

Control of a phosphate residual program involves adjusting soluble orthophosphate residuals in the boiler water by adjusting chemical feed rates. It is also important to adjust boiler water hydroxide (O) alkalinity (2P-M); the simple control of P alkalinity alone is not sufficient. As in all programs, proper levels of total dissolved solids, suspended solids, and silica must be maintained.

Phosphate residuals for any given system should be recommended based on boiler operating pressure; however, they should reflect the degree of control capability practical and the consistency of feedwater quality. Hydroxide alkalinity levels are similarly pressure related, and should be set according to individual conditions such as boiler silica levels expected.

Table 11.5 gives optimum limits at various boiler pressures. The values given in this table are guidelines; individual applications dictate the actual acceptable limits.

Phosphate-Polymer Programs

Simply stated, phosphate-polymer programs affect the proper calcium and magnesium precipitation reactions, then act to condition the resultant sludge. These programs result in cleaner boilers than are normally seen using a conventional phosphate program.

Phosphate-polymer programs are similar to the phosphate-residual and the phosphate-organic programs in that they use the same precipitation chemistry for calcium and magnesium. There are two important differences between the phosphate-organic and phosphate-polymer programs, however. These are the organic dosage requirements and the boiler water phosphate residual requirements (Table 11.6).

The organic portion of the phosphate-organic programs, is a blend containing various natural occurring organics. The polymers in the phosphate-polymer product line have a remarkable ability to alter the crystalline structure of the sludge (reaction products), preventing any seeding action and giving exceptional fluidity to the boiler water sludge.

Any use of the word or concept of chelation leads to a quick association with ethylenediaminetetraacetic acid (EDTA) and nitrilotriacetic acid (NTA). There are, however, many chemicals that exhibit chelation properties, including the polymers present in these products. Polymers, however, exhibit a much lower corrosion potential.

Applications

Phosphate-polymer programs are well suited to boilers with feedwater hardness levels up to 0.3 mg/L. (Hardness above 0.3 mg/L can be handled by phosphate-polymer treatment but at poorer economies. Usually, feedwater hardness >0.3 mg/L calls for corrective action.) For ion exchange softened feedwaters, except where iron is the sole or primary contaminant, phosphate-polymer programs normally give better results than conventional phosphate-organic programs.

Drum-Type Boilers Using Softened Feedwater[*]					
Boiler Water Component, mg/L	**Drum Pressure, psig (MPag)**				
	<450 (3.1)	**451–600 (3.1–4.1)**	**601–750 (4.1–5.2)**	**751–900 (5.2–6.2)**	**901–1000 (6.2–6.9)**
TDS (max)[†]	3000	2500	975	750	600
Phosphate (as PO_4)	30–60	20–40	20–40	15–25	15–25
Hydroxide (as $CaCO_3$)	250–300	250–300	50–200	50–150	50–100
Sulfite	30–60	30–40	20–30	10–15	Not recommended
Silica (as SiO_2) max[‡]	90	40	30	20	8

Drum-Type Boilers Using High-Purity (Deionized) Feedwater[*]						
Boiler Water Component, mg/L	**Drum Pressure, psig (MPag)**					
	<600 (4.1)	**601–750 (4.1–5.2)**	**751–900 (5.2–6.2)**	**901–1000 (6.2–6.9)**	**1001–1500 (6.9–10.3)**	**1501–2000 (10.3–13.8)**
TDS (max)[†]	Use same limits as for soft feedwaters	970	750	600	100	50
Phosphate (as PO_4)		20–40	15–25	15–25	5–10	5–10
pH		9.8–10.2	9.8–10.2	9.4–9.7	9.4–9.7	9.4–9.7
Silica (as SiO_2) max[‡]		30	20	8	2	1
Hydrazine (as N_2H_4)[§]		0.04–0.06	0.05–0.06	0.04–0.06	0.04–0.06	0.04–0.06

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[*] Heat release below 150 000 Btu/[h · ft²](473 kW/m²).

[†] The limits on TDS will vary with the design of the boiler and with the needs of the system with regard to steam purity. Despite TDS maximums, industrial boilers (as opposed to utility units) should not be operated above 50 cycles of concentration.

[‡] Silica may be carried at higher levels if there are no condensing turbines in the cycle. In any case, maintain an O Alkalinity/SiO_2 ratio of at least 3:1 to inhibit silica deposition.

[§] Hydrazine residuals in feedwater just ahead of boiler, for example, at economizer inlet.

Table 11.5 Common Control Limits for Phosphate Residual Programs versus Boiler Pressure

Requirements	Phosphate-Organic Programs	Phosphate-Polymer Programs
Organic dosage	The organic dosage is the amount needed to give a prescribed concentration (equivalent color numbers) in the boiler water and is not based on feedwater harness.	The phosphate dosage is directly proportional to feedwater hardness. Results depend on maintaining this relationship. Boiler water control tests, therefore, are meaningful only when feedwater hardness and boiler water concentration ratios are known.
Boiler water PO_4 residual	PO_4 residual (excess) in the boiler water is maintained simply to insure that all calcium hardness is precipitated as basic calcium phosphate. The boiler water must be tested on a filtered sample.	PO_4 residual provided by phosphate-polymer products serves primarily as an easy means of keeping product dosage at levels needed to maintain correct proportioning of polymer to feedwater hardness. In many cases, this will require higher boiler water PO_4 excess than that needed simply to insure proper calcium precipitation.

Table 11.6 Comparison of Phosphate-Organic and Phosphate-Polymer Programs

The phosphate-polymer programs have the same advantages and disadvantages as the conventional phosphate programs, with two exceptions:

1. Phosphate-polymer programs can provide much cleaner boilers than the conventional phosphate programs.
2. Much stricter control is required with these programs. Chemical dosages must be adjusted corresponding to feedwater hardness fluctuations to maintain the proper phosphate-to-hardness ratio.

Program Controls

Phosphate-polymer programs are controlled by phosphate residual readings on a filtered sample of the boiler water blowdown. In most cases, the phosphate control range will be established by normal product dosage calculations.

Special Considerations

At normal use dosages, the deposit removal capability of the phosphate-polymer products is dramatic. Deposit removal occurs by sloughing, which can block tubes and headers.

If, after inspecting a boiler, acid cleaning seems warranted, then the boiler should be cleaned. Do not try to substitute a phosphate-polymer treatment for an out-of-service cleaning. The odds are very much against such an approach succeeding. Online boiler cleaning is never recommended.

When a phosphate-polymer program is recommended for any boiler, except a new or a freshly cleaned one, special precautions should be taken. Where possible, schedule an inspection in 60 to 90 days to observe the condition of the boiler, particularly the lower areas, such as water-wall headers, near-horizontal tube runs, and the mud drum at the blowdown connection. Remove any accumulations of chip scale or sludge before putting the boiler back in service. During the first few months of operation on a phosphate-polymer program, increase the frequency of bottom blows, where applicable, to facilitate removal of materials sloughed from boiler surfaces. This should be done with greater frequency when turbidity levels increase in the boiler water.

If a phosphate-polymer program does not appear to be producing good results in an oil-contaminated system, change to a phosphate-starch organic product. The starch organic should help in handling the oil. The source of the oil contamination should be located and eliminated.

Very little, if any, change has been noted in the composition of sludge formed on a phosphate-polymer program as compared with sludge formed on a standard phosphate-organic program. Normal calcium and magnesium reaction products are formed, and normal interpretation of results can be made. There are visible differences, though. In the absence of dark lignin organics, the sludge is very light buff in color. The light film formed on metal surfaces may also appear grainy or granular. Light finger pressure will usually remove the light film, exposing the boiler metal. The volume of sludge will be proportional to the feedwater hardness levels.

Phosphate Programs—High Pressure Industrial Systems

Sodium phosphates provide the desired pH in boiler water, while controlling the presence of free sodium hydroxide, as shown by these hydrolysis reactions:

$$Na_3PO_4 \rightleftharpoons 3Na^+ + PO_4^{-3} \tag{11.24}$$

(trisodium phosphate)

$$Na_3PO_4 + H_2O \rightleftharpoons Na_2HPO_4 + NaOH \tag{11.25}$$

$$Na_2HPO_4 \rightleftharpoons 2Na^+ + HPO_4^{-2} \tag{11.26}$$

(disodium phosphate)

$$HPO_4^{-2} \rightleftharpoons H^+ + PO_4^{-3} \tag{11.27}$$

$$Na_2HPO_4 + H_2O \rightleftharpoons NaH_2PO_4 + NaOH \tag{11.28}$$

$$NaH_2PO_4 \rightleftharpoons Na^+ + H_2PO_4^- \tag{11.29}$$

(monosodium phosphate)

$$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{-2} \tag{11.30}$$

The practice of "congruent phosphate" treatment relies on the use of disodium and trisodium salts of phosphoric acid. The practice of "equilibrium phosphate" or "phosphate continuum" treatments relies on the use of trisodium phosphate with up to 1.0 mg/L of caustic soda (NaOH). Where the sodium (Na) to phosphate (PO_4) molar ratio in pure water is 3:1.

Controlling pH solely by sodium phosphate hydrolysis, bulk boiler water pH should never accidentally increase to levels aggressive to boiler steel. Equation (11.25) shows that the hydrolysis reaction of trisodium phosphate is self-limiting as this reaction does not proceed to dryness. As pH rises above 10, generation of hydroxide ions by hydrolysis decreases. It is theoretically impossible for a solution to reach a pH much above 12. If the Na_3PO_4 solution were to concentrate to 10 g/L, the pH would be 12.

Sodium hydroxide generated solely by this hydrolysis reaction is sometimes called "captive"; it will be "taken back" and revert to Na_3PO_4 at any sites of localized evaporative concentration. In theory, high concentration of NaOH in a confined area where solids might form is avoided, preventing caustic gouging of the metal. Thus, it was believed that maintaining a less than 3:1 Na/P molar ratio (coordinated phosphate control) in the boiler water would provide positive protection against the caustic concentration type of corrosion damage.

In Eq. (11.25), if water were to be removed by evaporation, the equilibrium would be forced to the left. In theory, upon evaporation to complete dryness, the residue would contain Na_3PO_4 free of NaOH. However, in the actual case of complete evaporation, even though Eq. (11.25) doesn't predict NaOH, due to the incongruent precipitation behavior of sodium phosphates, NaOH is formed and caustic stress corrosion cracking (SCC) is a potential issue at this highly stressed location. If these connections leak in service, then caustic SCC damage of the drum could occur, if the boiler water were allowed to contain free caustic.

Congruent phosphate chemistry control [sodium-to-phosphate molar ratio ($Na:PO_4$) less than 2.6:1, the “congruent ratio”] is required to prevent the formation of free hydroxide (OH^-) in this situation. This Na/P congruent ratio is temperature dependent and varies from 2.85:1 at lower pressures to 2.6:1 at higher pressures. Congruent phosphate control would still be the preferred phosphate chemistry to use in most industrial boilers that have mechanical tube-to-drum connections and the requisite feedwater purity unless they were having phosphate hideout issues.

In the past, in order to minimize the potential for caustic corrosion, treatment programs focused on maintaining the $Na:PO_4$ molar ratio less than 3. Control schemes varied. Plants employed congruent and coordinated phosphate treatments at various times. All of these phosphate treatment programs sought to restrict the boiler water sodium-to-phosphate molar ratio to less than three. These treatment programs were predicated on the belief that caustic corrosion posed a greater risk than acid corrosion. As boiler operating pressures increased, the susceptibility of these boilers to phosphate hideout especially on congruent control became greater, and the potential for phosphate wastage damage increased.

More recent data suggest that phosphate corrosion represents a significant risk too. The presence of up to 1 mg/L of free caustic ($Na:PO_4$ molar ratio >3) in the bulk water minimizes the possibility of phosphate hideout. These higher operating pressure boilers utilize all-welded construction (no tube-to-drum mechanical connections) and therefore, do not have to be concerned about susceptibility to SCC with this low level of free caustic in the boiler water.

EPRI updated its phosphate treatment recommendations in 1994 to create the Equilibrium Phosphate Treatment (EPT) and Phosphate Treatment (PT) programs. Congruent phosphate treatment was dropped from the guidelines in 1994, although it continued to be practiced in the utility industry. The EPT and PT programs limited the sodium-to-phosphate molar ratio to 3.0 + 1 mg/L NaOH (on the high end) and 2.8 (on the low end). At higher phosphate concentrations, the program was called phosphate treatment and at lower phosphate concentrations, it was called equilibrium phosphate treatment (Fig. 11.11.) The dividing line was the “equilibrium” phosphate level and plant specific. In practice, few plants determined their equilibrium phosphate level and instead relied on a hybrid treatment somewhere between EPT and PT.

The PT program is not similar to the coordinated phosphate program of the past. The EPT program was designed for units experiencing phosphate hideout, but that could not use all-volatile treatment (AVT) or oxygenated treatment (OT), due to the potential for feedwater contamination. The EPT program was essentially a low-level phosphate treatment (PT) program, with hideout setting plant specific limits for phosphate and hydroxide.

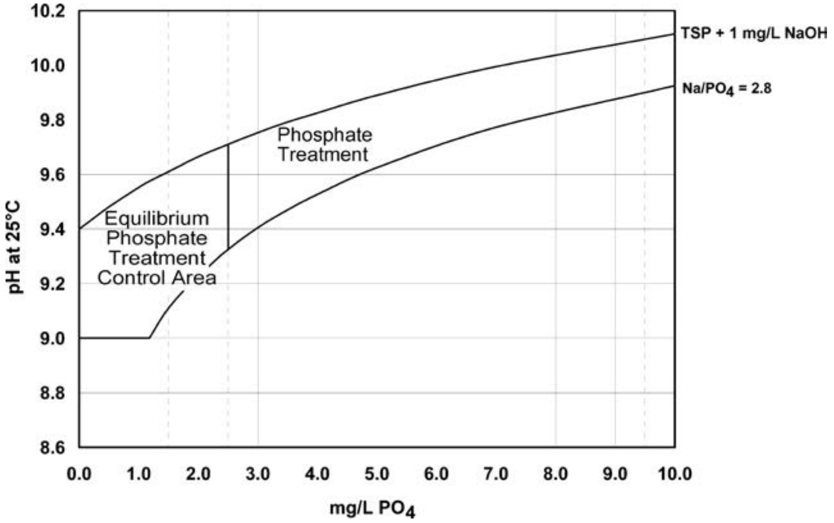

FIGURE 11.11 Traditional PT/EPT control chart.

In retrospect, the EPT program provided too little pH buffering at very low (<0.2 mg/L) phosphate concentrations. In addition, incorrect implementation of the limits at the plant level, resulted in several cases of subsequent hydrogen damage.

While an improvement over previous boiler pH control programs, EPRI sought to minimize the problems with the EPT/PT program and in 2004 issued its new recommendations, phosphate continuum (PC).

The continuum control strategies increase the minimum Na:PO_4 ratio to 3.0 with a maximum bounded by the trisodium phosphate (TSP) + 1 mg/L NaOH line. The minimum boiler water pH is 9.0 regardless of program type. The minimum phosphate is 0.2 mg/L. Plants attempting to control phosphate below this value are essentially using all-volatile treatment, and need to have feedwater purity to support AVT. Figure 11.12 illustrates the new limits.

The continuum control strategy eliminates the former dividing line between EPT and PT. Instead, the continuum program continues to transition as phosphate increases greater than 3 mg/L. Both areas are now combined to form the “phosphate continuum” (EPRI terminology). This new strategy requires tighter pH control, and product selection becomes critical. In general, only products with Na:PO_4 ratio greater than 3.0 are used. Disodium and monosodium phosphates are no longer typically used. In the electric utility industry note that the continuum treatment assumes feedwater can consistently meet the required purity guidelines. Plants with a source of

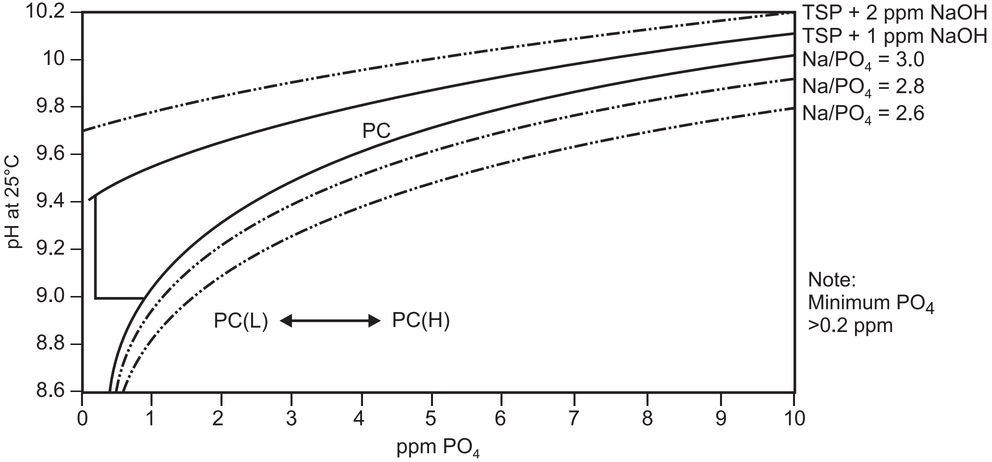

FIGURE 11.12 Phosphate Continuum control chart for high-pressure boilers.

sodium contamination, most often from the use of a two-bed demineralizer more common in the industrial steam generation systems, may have to feed disodium phosphate to obtain the desired Na:PO_4 ratio in the boiler water.

This new PC approach provides several benefits. It provides better pH control and buffering, greater tolerance of low-level feedwater contamination, reduced potential for phosphate attack (if hideout occurs), and easier control.

Chelates and Chelate-Polymer Programs

The nature of metal ions and how they behave must first be understood before discussing chelation and the use of chelating agents in the control of metal ions. When metal-containing compounds are ionized in water, the metallic component exists as a positively charged, freely moving ion in the solution. These free metal ions react to surround themselves with negative ions or polar molecules that are present in the solution. The number of such molecules or negative ions that coordinate with the metal ion varies, but for most metals it is usually four or six. These centers of activity of the metal ion may be termed reactive sites. In general, the reactions caused by free metal ions in solution are due to these reactive sites.

In an aqueous solution containing only a simple metal salt, the reactive sites will be occupied by water molecules. When materials are added that interact more strongly or compete more effectively than the water molecule for the reaction site, the sheath of water molecules is displaced, and the metal ion acquires new properties. An example of this is the reaction of copper ions with ammonia (Fig. 11.13).

The water molecules being held at the four reactive sites of the copper ion are displaced by ammonia. The ammonia forms a stronger attachment to the copper ion than does the water, so the resultant ammonia-copper complex is more stable. The ammonia can be displaced by adding some material capable of forming a still more stable complex with copper.

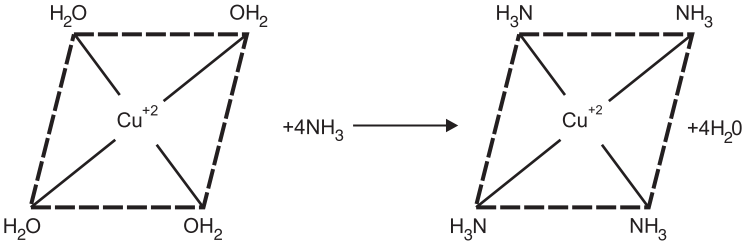

FIGURE 11.13 Copper ions with ammonia.

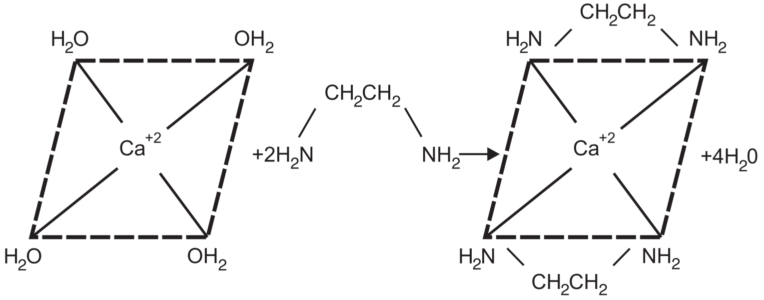

Figure 11.14 Calcium ions with ethylenediamine.

The common metal-complexing agents form complexes in which one molecule of the complexing agent coordinates with one reactive site of the metal ion. Thus, in Fig. 11.13, one ammonia molecule fills one reactive site of the copper ion. However, when the ammonia is replaced by ethylenediamine (a molecule made up of two amine groups connected by an ethylene bridge), a different type of compound results. The two complexing groups in the ethylenediamine molecule incorporate the copper or other metal ion, such as calcium or magnesium, into a ring-type structure (Fig. 11.14). The metal ion is said to be chelated, and ethylenediamine is termed a chelating agent. Thus, chelation may be defined as an equilibrium reaction between a metal ion and a complexing agent, characterized by the formation of more than one bond between the metal and a molecule of the complexing agent and resulting in the formation of a ring structure incorporating the metal ion.

Chelating agents control metal ions by blocking the reactive sites of the metal ion and preventing it from entering into its normal (and in many cases undesirable) reactions.

Metals chelated by chelating agents are still present in the system. They are inactivated because their reactive sites are blocked and, therefore, they can no longer undergo reaction or cause reactions in the system. This change in the nature of the metal ions is reflected by changes in their physical properties, which decreases the availability of the metals to react with other anions.

The word chelate derives from the Greek chele, meaning claw. The word chelate was probably chosen because of the structure of the molecule, which holds the metal that has been chelated tightly in a ring structure. The resulting complex is quite soluble and will not permit the hardness metals, calcium and magnesium, to deposit in the boiler as carbonates or sulfates. Although this complex is quite stable under boiler conditions, strong competing anions such as phosphate, silicate, and hydroxide can form insoluble precipitates with the hardness ions in the presence of chelates. Since this type of reaction is an equilibrium between the metal ion and the chelate, a slight excess (residual) of the chelate is required to maintain the metal ion in solution. If the residual chelate is excessive, however, corrosion of the boiler metal may result.

In boiler applications, the two most common chelates used are ethylenediaminetetraacetic acid (EDTA) and nitrilotriacetic acid (NTA).

Applications

Chelating agents must be fed continuously into deaerated feedwater. Chelating agents do not react successfully under oxidizing conditions, because either the chelating agent or the resulting complex breaks down. The presence of any oxygen significantly increases the potential for corrosion by the chelating agent; therefore, an oxygen scavenger must be fed ahead of the feed point of the chelating agent.

Concentrations of chelate residuals, both NTA and EDTA, should never exceed 20 mg/L (as $CaCO_3$) in the boiler water, because corrosion is a definite possibility if this range is exceeded. Control for all products is by measurement of residual (unreacted chelate expressed as $CaCO_3$). Suggested control ranges are shown in Table 11.7 as a function of boiler pressure. Where the possibility of concentration mechanisms or film boiling exists in a new or existing boiler, chelates should not be used, unless a hydrogen corrosion study has been done to determine their effect on the boiler.

Special Considerations

Alkalinity requirements of the boiler water are the same as those for a conventional phosphate-organic treatment program. The lowest practical O alkalinity is 120 mg/L. O alkalinity is important and must be determined by the barium chloride titration method. P alkalinity alone is not a sufficient control parameter, because it includes one-half of the carbonate alkalinity as well as the hydrate alkalinity.

Silica control is the same whether a chelating agent or a phosphate-polymer is used. Because the major purpose of silica control is to reduce steam contamination (and turbine fouling), boiler pressure is the criterion for determining the maximum silica limit. Operating experience does not indicate any noticeable positive benefits of chelating agents on silica.

Cycles of concentration should be controlled to minimize the breakdown of chelated complexes at the heat transfer surfaces.

Boiler Pressure, psig (MPag)	Chelate Residual, mg/L as $CaCO_3$
400 (2.8)	4–8
401–600 (2.8–4.1)	3–6

Table 11.7 Suggested Control Ranges for Chelate Residuals

Chelates are organic molecules and are therefore subject to thermal degradation. Although the chelated metal ions are somewhat thermally stable, breakdown of the complexes can occur, with the EDTA complexes being less stable than the NTA complexes. When thermal breakdown of the complex occurs, the metal ion is released and will precipitate on the heat transfer surfaces as scale. Thermal breakdown is a function of temperature and time. If the residence time in the boiler is minimized, the formation of scale will also be minimized. The residence time in the boiler can be minimized by controlling the concentration to 50 cycles or less. Additionally, the residual chelate is more subject to thermal degradation than is the chelated complex. This degradation is dependent on temperature, time, and oxygen. This is particularly true of the EDTA molecule. The initial breakdown products of EDTA are weak chelates but are not detected in the test for residual chelate. These breakdown products can be corrosive to the boiler metal.

In some cases, chelate products are formulated with polymers. This combination can be very corrosive to boiler metal, particularly when the boiler makeup water is demineralized where there is no hardness for the chelate to complex. The corrosion from the combination of chelate and polymer can be more severe than either chelate or polymer alone.

Dissolved solids should be maintained at the same level as with a conventional phosphate-organic treatment program. Products containing antifoam will provide additional protection, but total dissolved solids must still be controlled as with a conventional program.

Continuous feed of any chelating agent to the feedwater is necessary. Accurate control is essential, so a chemical pump and solution or day tank are required. Chelating agents are corrosive to mild steel at high concentrations (above 5%) and temperature greater than 100°F (38°C). Therefore, chelate solutions should be fed from either stainless steel or polyethylene feeding equipment.

Application of chelates should be to the feedwater line only. A quill injector, stainless steel piping, and shut-off valve must be used at the point of entry into the feedwater line. The feedwater at the point of chelate injection must be completely deaerated and should carry a residual oxygen scavenger.

Online cleanup of an operating boiler should not be recommended, because sloughing deposits can cause blocked tubes and subsequent tube failures. A dirty boiler should be acid cleaned offline by a qualified cleaning company.

Applied product dosages should be no greater than the theoretical dosage required to complex all feedwater hardness and to supply desired chelate residual in the boiler. If the chelate residual does not appear in the boiler at this theoretical dosage, do not increase chemical feed rate, unless the variables for the dosage calculation have changed (i.e., feedwater hardness has increased or boiler concentrations have decreased). The residual will appear in time as long as the theoretical dosage is maintained. Increasing chemical feed in lieu of changes in theoretical demand will cause more rapid sloughing of deposits from surfaces, which may result in circulation restrictions and subsequent tube failures.

All-Polymer Programs

Nalco was the first company to introduce all-polymer boiler internal treatment programs to the market (1980). Designing an effective all-polymer boiler treatment is very complex. There are a number of critical chemical and physical properties that must be considered and evaluated when developing an all-polymer program:

- The polymer structure and its molecular weight profile
- Hardness complexing ability
- Stability under boiler operating conditions
- Dispersant capacity
- Oxygen stability
- Solubility of the polymer-hardness complex
- Breakdown mechanism, products, and temperature
- Toxicity of breakdown products and effects on boiler
- Corrosiveness of polymer
- Regulatory status

All-polymer programs contain no chelants, phosphates, or phosphonates and require no supplemental dispersant to be effective. They function by dispersing particles such as iron oxides and boiler sludge and by complexing individual hardness ions to prevent the precipitation of mineral scales.

The polymers used for boiler treatment are formed from monomers having carboxylic acid functional groups and are called polycarboxylates. Acrylic acid and methacrylic acid are the carboxylate monomers that Nalco uses in its boiler polymers. Some polymers also contain styrene sulfonate monomer. The polycarboxylates are anionic in the alkaline pH range.

Polycarboxylates have an attraction toward the surfaces of particles in the boiler water and can adsorb on those surfaces. The particles can be iron oxides or mineral scales and boiler sludge that precipitate from solution inside the boiler. When the polymers adsorb on the surfaces of particles, they enhance the surface electrical charge and increase the repulsive force between the particles. The large polymer molecules also form a physical coating on the particles that reduces the possibility of agglomeration or deposition on the heat transfer surfaces. This mechanism is called dispersion, and the polymers can be

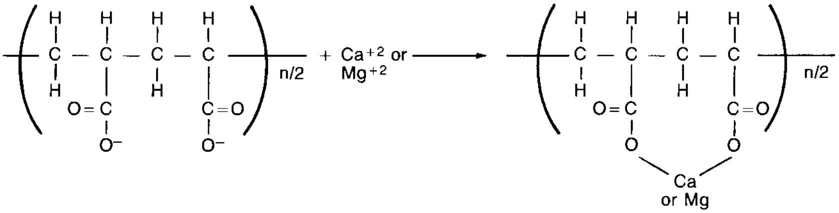

FIGURE 11.15 Polymer solubilization mechanism.

called dispersants or sludge conditioners. Polymers are uniquely effective dispersants, but small molecules such as chelants do not function in this manner.

All-polymer programs inhibit hardness scale formation by maintaining the solubility of calcium and magnesium ions. The solubilization mechanism involves complexation of hardness by the carboxylate functionality of the polymer. The reaction can be simply illustrated as shown in Fig. 11.15.

The carboxylates form strong bonds with the hardness ions. Since the polymers have many possible binding sites and are flexible molecules, the binding is maintained even at high temperature. While this binding is excellent for inhibiting the formation of hardness scale under normal conditions, it does have a drawback. During hardness excursions (e.g., softener breakthrough or condensate contamination), some types of polymers can be overwhelmed by excessive calcium concentration, and a neutral calcium polyacrylate complex can precipitate from solution. This calcium polyacrylate precipitate can form adherent deposits on the boiler heat transfer surfaces. This precipitation process removes the polymer from solution, and mineral scales such as magnesium silicate can form rapidly during calcium polyacrylate deposition episodes.

A copolymer of acrylic acid and styrene sulfonate was developed to avoid the calcium polyacrylate problem. The sulfonate group does not bind hardness and maintains a negative charge on the polymer even in the presence of high concentrations of calcium. The negative charge keeps the polymer soluble so it does not become incorporated in the scale. The soluble polymer maintains its dispersant activity and inhibits the deposition of hardness scales that may be precipitating during the upset condition.

Applications

Although far less aggressive than chelants (EDTA and NTA), polymers can bind individual iron ions and participate in corrosion reactions. These reactions are greatly accelerated by high flow rate or turbulence. Care must be taken to dose polymers properly, especially in systems with very low hardness or demineralized feedwater. Feed point location is also important, and injection of neat polymer products directly in front of turbulent areas such as pumps or elbows should be avoided. Corrosion caused by chelants or polymers can be detected and gauged by the use of the Fe^{+2} test.

Polymer dosage should be based on a statistical upper control limit, not merely on average total feedwater hardness. Severe hardness upsets or underdosing of acrylate/acrylamide polymers (20% of recommended) may result in the formation of calcium polyacrylate deposits. If a major upset (outside the control limit) occurs, product feed must be increased to recommended levels, and blowdown must be increased accordingly. Copolymers of acrylic acid and styrene sulfonate will not form calcium polyacrylate, but both dosage and blowdown should be increased during hardness upsets.

Fifty cycles of concentration should be considered the maximum for industrial boilers. Over cycling does not allow for proper purging of boiler water solids, which can be extremely high during upset conditions. All-polymer programs are organic in nature and therefore susceptible to thermal degradation, which is a function of temperature and time. Operating at high cycles can cause thermal degradation of polymers and poor performance. This is particularly true for iron deposit formation. If operation above 50 cycles is required, the boilers will require high-purity feedwater (demineralized) and condensate polishing or filtration to remove iron particulates. Only high stability polymers should be used. The ASME guidelines for boiler water quality (Consensus on Operating Practices for the Control of Feedwater and Boiler Water Chemistry in Modern Industrial Boilers, latest edition) should be followed.

Program Controls

Polymer programs should be controlled by testing for the active polymer, or by a combination of testing for traced fluorescence technology (TRASAR® technology) and active polymer. Traced fluorescence technology is a nonvolatile, nonprecipitating, and nonreactive chemical that can be fed into the boiler feedwater. The concentration of traced material can be measured by the fluorescence of a water sample. The ratio of the concentration of traced material in the boiler water divided by the traced material concentration in the feedwater is the cycles of feedwater concentration in the boiler water. Traced fluorescence technology testing can be used as a routine method for grab sample analysis or online control.

When using traced fluorescence technology as a routine control method, the active polymer concentration in the boiler water should be tested to confirm good polymer recovery. The organic polymers can be subject to some thermal degradation, especially in boilers operating above 600 psig (4.1 MPag). Oxygen ingress can cause polymer degradation in any boiler system. Occasional polymer recovery testing will detect any problems with thermal or oxygen degradation and prevent performance problems.

Polymer recovery testing is accomplished by measuring product concentration by traced fluorescence technology and comparing that value to product concentration measured by active polymer testing. In boilers operating normally, the boiler water product concentration by active polymer testing should be 80 to 100% of the traced fluorescence technology product concentration.

Advantages and Disadvantages

All-polymer programs offer several advantages over other scale control programs, such as:

- Produce the cleanest heat transfer surfaces and highest boiler efficiency
- Transport 100% of hardness through the boiler
- Excellent iron and sludge dispersion to maintain cleaner heat transfer surfaces
- Can be applied to virtually any type of boiler, including waste heat boilers
- Copolymers of acrylic acid and styrene sulfonate do not form calcium acrylate deposits when underdosed because of feedwater hardness upset conditions
- The program is nonvolatile, so it is safe for turbine operation
- Program control tests are easy
- The polymers do not interfere with hardness testing
- FDA/CFIA (Canadian Food Inspection Agency) approved
- Traced fluorescence technology compatible

Disadvantages include:

- Limited to boilers operating at pressures below 1000 psig (6.9 MPag)
- Feedwater hardness limits of 0.02 to 3.0 mg/L as $CaCO_3$
- Can be corrosive if overfed
- Can release chip scale (do not feed to dirty boilers)

Special Considerations

Any polymers containing acrylamide will contribute significant concentrations of ammonia to the steam from the thermal hydrolysis of the amide. Nalco has moved away from using such polymers for boilers. High ammonia concentrations can result in an artificially high pH in the final condensate. If, when using an acrylamide-containing polymer, condensate treatment is decreased and the condensate pH remains high, it is imperative to check condensate iron values and to check system pH at intermediate locations, not just at the bulk condensate return.

Ammonia release from acrylamide-containing polymers can be corrosive to any copper alloys present in the feedwater and condensate system. Generally, 300 to 500 µg/L of ammonia can be tolerated in a copper alloy-containing feedwater system, depending upon dissolved oxygen content. If higher oxygen concentrations are present, lower concentrations of ammonia are required to reduce copper corrosion.

All-polymer products contribute sodium to steam generation systems; therefore, extreme care should be used when applying these products to higher-pressure systems as an overlay to coordinated phosphate or congruent phosphate programs.

If the boiler is operated properly and no carryover exists, then polymers present no steam contamination issues. However, in certain types of systems (refineries, ammonia plants, etc.), economic risks are present in the form of poisoned catalyst if boiler water is carried over into the steam. In systems containing turbines, boiler water carryover can damage or impair turbines. To prevent problems in the areas of steam use, it is important that the total system be understood before recommending a treatment program. This includes knowledge of steam purity and the system needs for steam quality, as well as the effects of known contaminants on the process.

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CHAPTER 12

Turbines

Steam turbines are the workhorse in power plants as well as in industrial steam systems. The major use of steam is motive power, and this is the sole use in the utility industry. Even in moderate-sized industrial plants where the chief reason for generating steam is for process requirements, steam may be put through a turbine at high pressure, with the exhaust steam then being used for process needs. Turbines are the prime movers because they are compact and efficient. These prime movers may be used for direct drive of pumps, compressors, and other mechanical devices, or they may be connected to a generator to supply electrical energy.

Turbine Mechanics

In a steam turbine, the working fluid (in this case steam at high temperature and pressure) contains potential energy. The potential energy of the working fluid is converted into mechanical work through expansion in a nozzle and impact and/or reaction with a blade, and the mechanical work of many sets of blades attached to a shaft produces rotational power.

Water is converted to steam by the application of heat. As heat is supplied to water, temperature increases until boiling occurs [212°F (100°C) at atmospheric pressure]. At the boiling point, temperature remains constant until all water is converted to vapor (saturated steam). Although it requires only 1 Btu/lb for each degree Fahrenheit of temperature increase [4.18 kJ/(kg·°C)] to the boiling point, 970 Btu/lb (2255 kJ/kg) are required to change water at 212°F (100°C) to saturated steam. If the pressure of the boiler water is increased, the boiling point also increases, requiring application of still more energy. Steam at higher pressure has a higher temperature and contains more energy. As pressure increases, the amount of heat required to raise water to the boiling point increases, while the amount of heat necessary to vaporize the water decreases. Eventually at a pressure of 3200.1 psia (22.1 MPaa) and 705.1°F (373.9°C), water turns to steam without boiling; this is called the critical point. Turbines that operate at temperatures and pressures above the critical point are called supercritical units.

The problem with saturated steam, regarding turbines, is that it can contain water droplets, which can cause friction losses, erosion, and other problems. To dry saturated steam after vaporization, additional heat may be added to the steam, increasing its temperature; this process is called superheating. The enthalpy (potential energy) of steam increases by the amount of heat added. Superheating not only increases energy content, but also permits transporting steam through piping with less condensation.

The term enthalpy denotes the heat content of water or steam expressed in Btu/lb (kJ/kg). Enthalpy is a measure of the potential energy in the fluid. Steam tables have been developed to relate the properties of steam and water at various temperatures and pressures, and are available from the American Society of Mechanical Engineers (ASME) and other industry sources. Steam data can also be organized graphically in what is known as a Mollier chart.

To convert the steam's energy into work, steam must go through a thermodynamic fluid cycle that combines expansion, compression, heat input, and heat rejection. Steam turbines are based on the Rankine cycle (Fig. 12.1). At the end of the cycle, condensate is simply pumped back to the boiler to begin the cycle again. The role of the steam turbine is to expand the steam. As it expands, or drops in pressure, through a small opening or nozzle, it accelerates and forms a high-speed jet. Harnessing this momentum in a rotating blade provides mechanical work.

Turbines are fundamentally classified as impulse or reaction type based on how the steam expands through a nozzle and impacts a blade. In the simple single-stage turbine, steam is directed through a series of carefully shaped nozzles onto blades, or buckets, fixed at the circumference of the disk attached to the turbine shaft. This is known as the impulse stage. As steam leaves the rotating blades, a second set of stationary nozzles may be used to collect it and redirect it onto a second set of blades, or buckets, in which case the second set

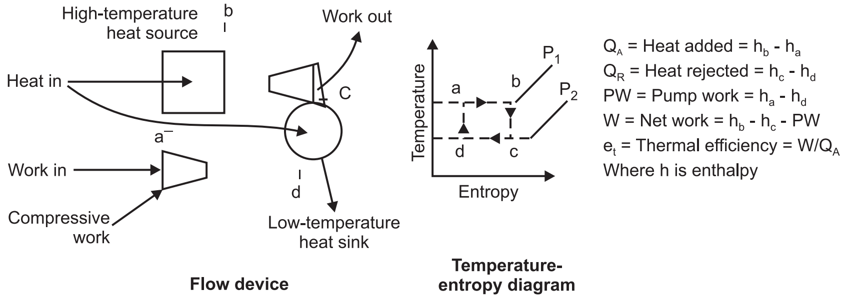

FIGURE 12.1 Rankine cycle. (*Courtesy of POWER Magazine, all rights reserved.*)

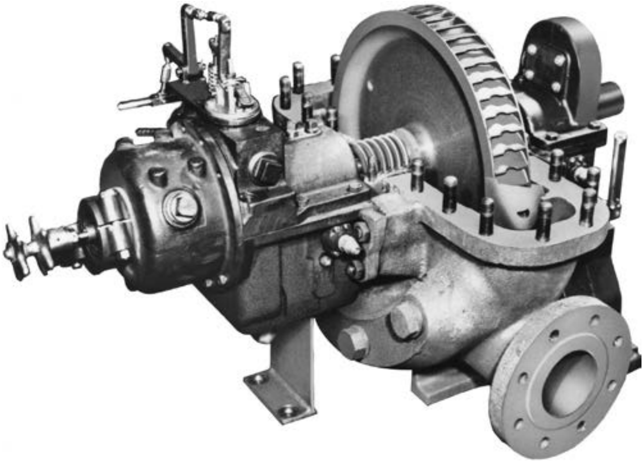

Figure 12.2 Simple solid wheel turbine commonly used to drive auxiliary equipment such as boiler feedwater pumps and rotary compressors.

of nozzles and blades is called a reaction stage. Under ideal conditions, the steam jet does the most work when the blade speed is half the steam speed. Most turbines contain multiple stages, in practice, combining impulse and reaction stages. A simple single-stage turbine is shown in Figs. 12.2 and 12.3. A multiple-stage utility turbine is shown in Fig. 12.4.

There are two basic categories of steam turbine operation: condensing, when exhaust steam discharges to a condenser at subatmospheric pressure and noncondensing, where steam exhausts into process steam headers under pressure. In the condensing turbine application, a vacuum is maintained in the condenser by steam-jet air ejectors or a mechanical vacuum pump. Shaft-sealing steam is applied to the turbine glands to prevent air from entering the seals and destroying the vacuum.

Turbine operation and designation are further classified as to the flow of steam through the turbine; flow patterns include straight flow, reheat, and extraction. In straight flow systems (Fig. 12.5), steam is directed by nozzles through the entire bank of turbine stages to exhaust. Reheat turbines, most commonly used in the electric utility industry, (Fig. 12.6) gain efficiency by discharging the main steam flow at one (single reheat) or two (double reheat) intermediate stages for reheat in the boiler, with that high temperature steam being returned to the next stage of the turbine for further expansion. In extraction turbines, steam is extracted from the main steam flow at one or more points for process use, with the balance passing through to exhaust (Fig. 12.7). Steam turbines come in a wide range of sizes. Capacities begin at less than 0.75 kW (1 hp) and extend up to more

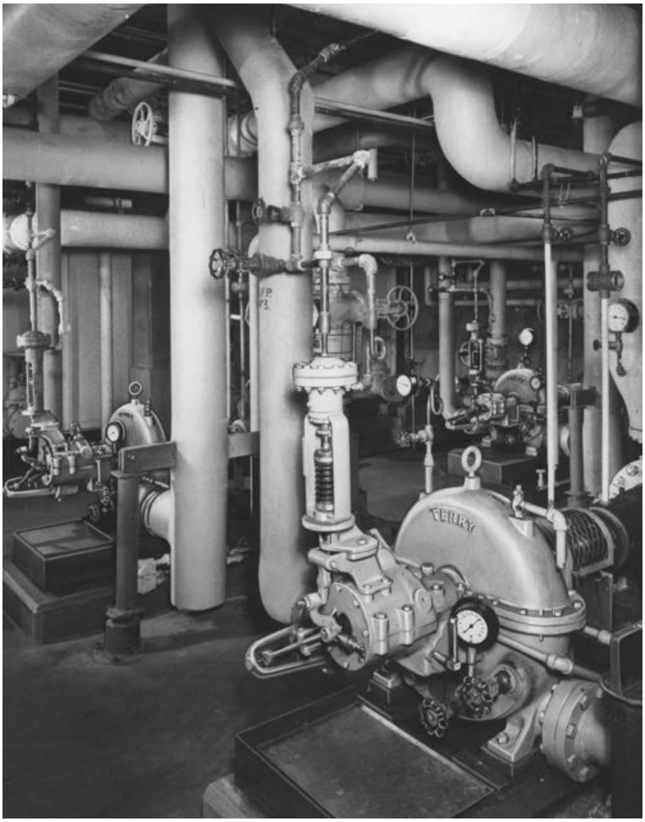

Figure 12.3 A typical plant installation of a single-stage turbine. (*From Power Special Report, "Steam Turbines," June 1962, Courtesy of Terry Corporation*.)

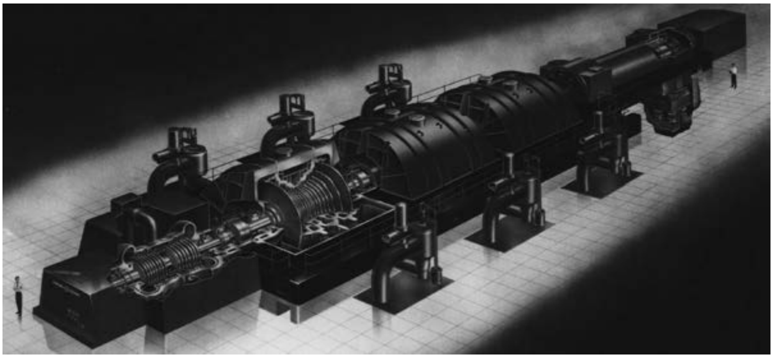

Figure 12.4 Large turbogenerator typical of nuclear power plants. Cutaway section shows high-pressure and low-pressure turbine blades. (*From Power Special Report, "Steam Turbines," June 1962, Courtesy of General Electric Company*.)

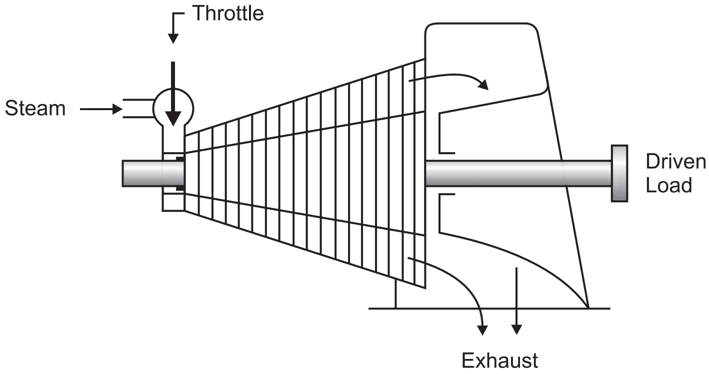

FIGURE 12.5 Straight-flow turbine. (*From Power Special Report. "Steam Turbines," June 1962*.)

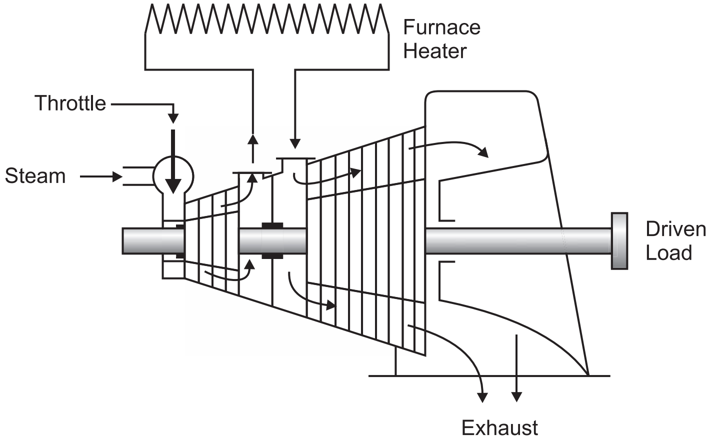

FIGURE 12.6 Reheat turbine. (*From Power Special Report. "Steam Turbines," June 1962*.)

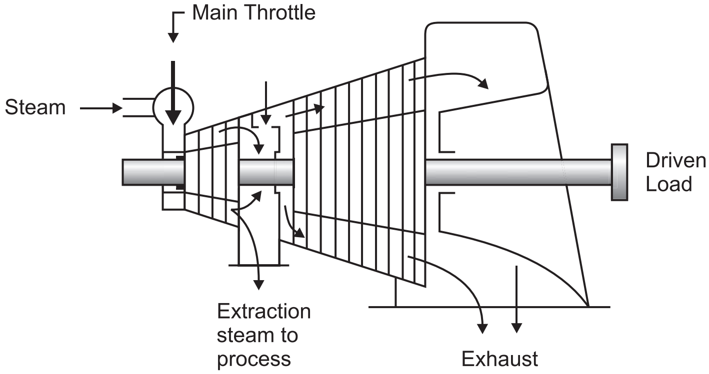

FIGURE 12.7 Single automatic extraction turbine.

than 1300 MW for generator drives in the largest central electric generating stations. Larger turbines may have two shafts, side by side, driving two generators, known as cross compound units.

Turbine Problem Areas

Solid particle erosion (SPE) of high-pressure (h-p) and intermediate-pressure (i-p) turbine internals, particularly blades and nozzles, is a common problem for boilers that produce steam at temperatures above 900°F (482°C). The common low-chromium alloy boiler materials, used in superheater and reheater tubes, headers, and piping forms a high-temperature oxide in service. This oxide scale can exfoliate from boiler tubes and steam leads once a critical thickness is reached and becomes entrained in the steam flow to the turbine, eroding components in the steam path. Temperature changes associated with startup, shutdown, and load cycling service, typically provide stresses on the oxide layer relative to the base material to initiate exfoliation. The effects of SPE include efficiency losses and susceptibility of damaged components to the possibility of mechanical failure and catastrophic loss.

Another troublesome type of turbine problem is related to the accumulation of material on turbine blading. This can be due to mechanical carryover of boiler water and its associated constituents into the steam or to the vaporous transport of selected species out of the boiler water into the steam. Deposits in the inlet high-pressure end of the turbine generally affect steam throughput. This is typically the result of high levels of mechanical carryover out of the boiler for most industrial turbine installations. Deposits can also cause vibration problems in the turbine and impair control valve operation.

For electric utility boiler systems operating above 2400 psig (16.5 MPag) drum pressure, copper oxide in its more oxidized form (CuO), which has a significant vaporous solubility in saturated steam, can result in deposits in the high-pressure turbine, restricting unit capacity. Strict control of feedwater oxidation-reduction potential (ORP) can minimize this transport of copper. Silica is the other boiler water constituent that has appreciable vaporous solubility in saturated steam above 600 psig (4.1 MPag), and must be limited in concentration in the boiler water to avoid vaporous transport to the turbine and subsequent deposition (typically in lower-pressure stages).

Lesser levels of impurities in the steam, but still above the solubility limit for those constituents in the phase transition zone (PTZ) of the low-pressure turbine section, can lead to deposition and corrosion problems. Acceptable steam purity for an industrial condensing steam turbine is typically less than 10 μg/L sodium in the steam and less than 20 µg/L sodium in the steam for an industrial backpressure turbine. Some turbines are more sensitive to deposition than others, and new turbine installations may have even more restrictive steam purity guarantee limits. Measurement of the sodium concentration in steam is commonly used as a method of determining steam purity. Sodium is a common element in boiler water and online instrumentation in the form of a sodium selective ion electrode is capable of reliably measuring sodium to sub µg/L levels.

Stress corrosion cracking (SCC) and corrosion fatigue are the two most common potential failure mechanisms associated with inorganic impurities (typically chlorides, sulfates, and caustic) in steam. The extent of the problem depends greatly on the purity of the steam and the blading and blading attachment design details. Most susceptible are the L-1 and L-0 (last stage) (Fig. 12.8). The transition between dry and wet steam, formerly known as the Willson line, now termed as PTZ, occurs here. The possible effects on the turbine of organic contaminants in steam are not nearly as well understood and are currently the subject of research activities in the industry.

Chemical compounds precipitate and deposit, when their concentration in superheated steam exceeds their solubility. Since solubility in dry steam decreases as steam expands, this mechanism is most common on components operating near the dry/wet transition (PTZ).

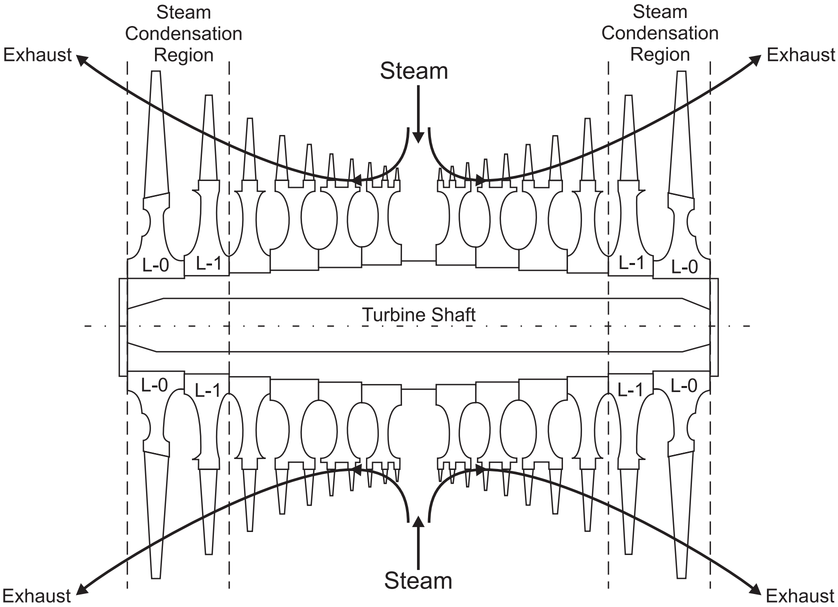

FIGURE 12.8 Illustration of the L-1 and L-0 placement on a turbine. (*Courtesy of POWER Magazine, all rights reserved*.)

In steady-state operation, deposition from dry steam involves three simultaneous processes: precipitation from expanding steam, deposition on a surface, and erosion of the deposit. Under load change, shutdown, and startup conditions, a deposit can be washed away by moisture. When steam composition changes from higher to lower concentration, a deposited salt can start dissolving back into dry steam and be carried away. A deposit can also be physically dislodged from surfaces and transported further forward into the steam system.

For some time, the turbine corrosion issues (stress corrosion cracking and corrosion fatigue) in the PTZ were thought to be associated with the online steam purity conditions and turbine operation. More recent work though, has shown that the corrosion mechanisms are initiated during out-of-service conditions when the system is exposed to moisture or humidity and oxygen at which time pitting may occur. These are then propagated into the cracking phenomena in subsequent operation. The current recommendation to minimize this potential damage mechanism is to apply a controlled out of service environment for the turbine via continual nitrogen purging or the application of a dehumidified air protection system.

Control of impurity sources, adequate treatment to remove impurities, and proper sampling and chemical analysis are essential to corrosion control. Chemistry control is one of the most important

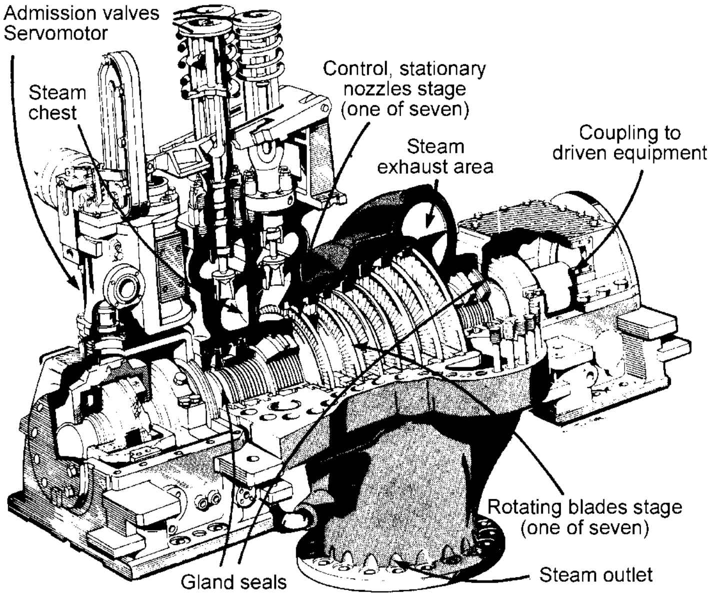

FIGURE 12.9 A backpressure multistage steam turbine. (*Courtesy of POWER Magazine, all rights reserved.*)

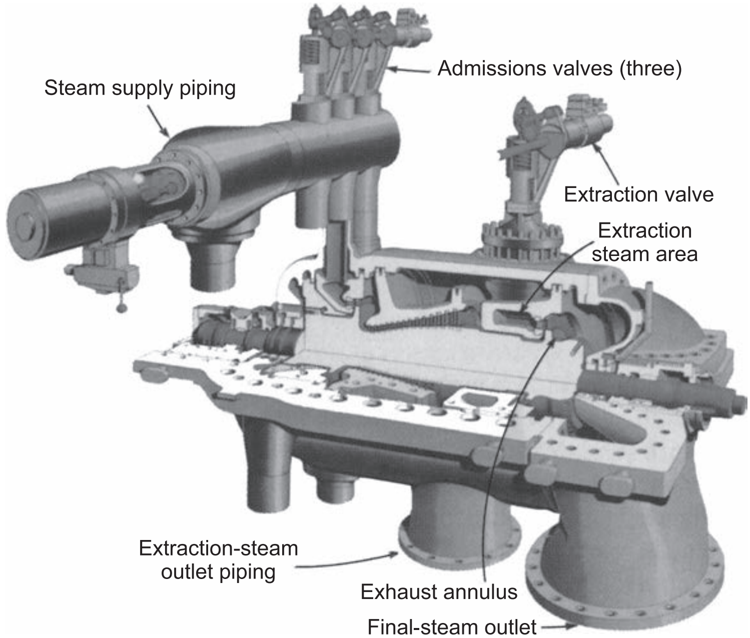

FIGURE 12.10 A single-extraction multistage steam backpressure turbine. (*Courtesy of POWER Magazine, all rights reserved*.)

requirements during operation. In particular, direct analysis and control of steam chemistry is necessary, because boiler water specifications do not guarantee acceptable turbine steam.

Finally, smaller steam turbines (Figs. 12.9 and 12.10) are used to drive critical process equipment, including pumps, compressors, fans, and paper machines. Efficient mechanical drives are critical to an optimized steam system and plant energy balance. High steam temperatures, pressures, and speeds characterize turbines for mechanical drives. Improper steam purity can similarly adversely affect their availability and reliability.

In mechanical drive applications, steam turbines compete with electric motors. Advantages commonly attributed to turbines include: flexibility to use multiple inlet and exhaust pressure levels, inherent variable speed operation, operation independent of electric power supply, and spark-proof controls for hazardous fluid duty. The relative value of thermal-to-electric energy determines the motor/turbine selection decision.

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CHAPTER 13

Condensate Systems

A primary objective in the successful operation of any steam generating system is to maximize its overall efficiency and reliability, while minimizing problems related to water and steam purity. One of the greatest factors in achieving this objective is the amount and purity of condensate returned to the boiler as feedwater. Returned condensate, being condensed steam, is typically free of impurities and has a relatively high heat content, making it ideal, both economically and technically, for boiler feedwater.

Economically, the more condensate returned, the less makeup water required, thereby saving on both water and feedwater pretreatment costs. The high purity of condensate allows the boiler to operate at higher cycles of concentration while maintaining conductivity standards, thereby reducing costly water and energy losses to boiler blowdown. The higher heat content of condensate [158 Btu/lb at 190°F (367 kJ/kg at 88°C)] as compared to makeup water [28 Btu/lb at 60°F (65 kJ/kg at 16°C)] directly reduces the fuel requirements of the boiler to convert feedwater into steam.

Technically, the high purity of condensate reduces the overall scale-forming tendency of boiler feedwater, regardless of the sophistication of the makeup water pretreatment system. This results in cleaner heat transfer surfaces and optimal heat transfer rates. Higher purity feedwater reduces the possibility of boiler tube failure due to excessive scaling.

To realize the benefits of a condensate return system, a program of corrosion control must be implemented. Left untreated or treated improperly, condensate can become very corrosive to plant piping and equipment. The resulting products of corrosion can enter the feedwater and form harmful, tenacious deposits on boiler heat transfer surfaces. The lack of condensate corrosion control can ultimately result in the loss of heat transfer efficiency and ruptured boiler tubes, a leading cause of unscheduled plant shutdowns.

Causes of Condensate System Corrosion

It is a myth that pure condensed steam is noncorrosive to most metals. Condensate formed from extremely pure steam has a conductivity of less than 1 µS/cm and a pH of 6.5 to 7.0. These are the characteristics of pure water. At a pH of 6.5 to 7.0, condensate is very aggressive to most metals. The presence of very small amounts of contaminants in the steam or leaking into the liquid condensate can further depress the pH and accelerate the corrosion rate of most ferrous and nonferrous metals.

The primary contaminants that lead to increased condensate corrosion are gases carried in the steam from the boiler. These gases dissolve in the condensate to form a solution corrosive to most metals. Carbon dioxide and oxygen are the gases most corrosive to ferrous metals; the combination of ammonia and oxygen poses the greatest corrosive threat to copper alloys. In certain instances, sulfur dioxide, hydrogen sulfide, and organic acids result in very corrosive condensate.

Carbon Dioxide

The gas most commonly associated with condensate corrosion is carbon dioxide (CO_2). Although CO_2 can be found in many waters in the free state, it is normally removed through pretreatment and deaeration. The major source of CO_2 in the steam is the thermal breakdown of bicarbonate (HCO_3^-) and carbonate (CO_3^{-2}) alkalinity present in the feedwater. At boiler temperatures and pressures, the following alkalinity reactions occur:

$$2NaHCO_3 \rightarrow Na_2CO_3 + CO_2\uparrow + H_2O \tag{13.1}$$

$$Na_2CO_3 + H_2O \rightarrow 2NaOH + CO_2\uparrow \tag{13.2}$$

The breakdown of bicarbonate [Eq. (13.1)] proceeds 100% to completion. Carbonate breakdown [Eq. (13.2)] proceeds from 10 to 90% to completion, depending on the temperature, pressure, and holding time of the boiler. The CO_2 liberated in both reactions exits the boiler with the steam.

Carbon dioxide is not harmful until it dissolves in the condensate. As it dissolves, it forms carbonic acid (H_2CO_3):

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \tag{13.3}$$

The extent to which carbon dioxide dissolves is predicted by Henry's law, which states that the quantity of gas that can dissolve in a liquid is proportional to its partial pressure in the contacting vapor or gas phase. The solubility of CO_2 is also influenced by temperature and pressure, since gases are less soluble in liquid as the temperature approaches or exceeds the boiling point. Finally, CO_2 solubility is influenced by pH, since pH determines whether the CO_2 remains as a gas (with a vapor pressure) or converts to the bicarbonate salt (without a vapor pressure). All together, these three principles determine the vapor/liquid (*V/L*) distribution ratio for CO_2 at the specific conditions present. (*V/L* ratios will be discussed later with neutralizing amines.)

Since condensate is extremely pure, even small quantities of carbonic acid, a relatively weak acid, can significantly lower condensate pH and correspondingly increase its corrosivity. Figure 13.1 shows that as little as 1 mg/L of CO_2 in the steam can depress condensate

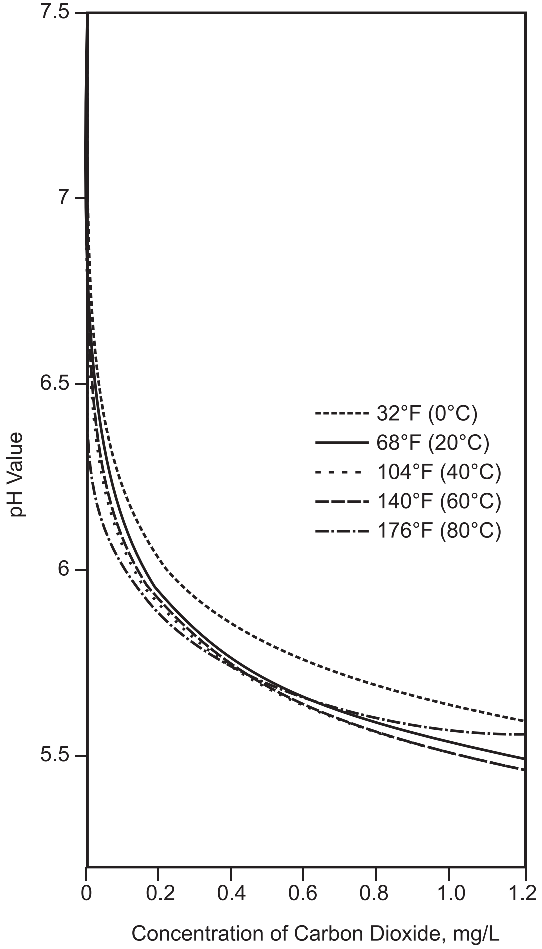

Figure 13.1 pH versus CO_2 concentration in pure water at various temperatures.

pH from 7.0 to 5.5 at typical condensate temperatures. It is apparent that high alkalinity feedwater will produce very corrosive condensate.

The corrosion reaction of carbonic acid on iron produces ferrous bicarbonate [$Fe(HCO_3)_2$] and hydrogen gas:

$$Fe + 2H^{+} + 2HCO_3^{-2} \rightarrow Fe(HCO_3)_2 + H_2\uparrow \qquad (13.4)$$

The ferrous bicarbonate is highly soluble and has no passivating effect. It can be carried away with the condensate, leaving behind an area of obvious metal loss. The ferrous bicarbonate is not particularly stable, and various secondary reactions are likely to take place, resulting in the formation of ferrous and ferric oxides, hydroxides, and carbonates.

Carbonic acid attack is characterized by a thinning or grooving of metal surfaces in contact with the corrosive condensate. In the absence of oxygen, carbonic acid generally causes a rather smooth surface, where the iron has been dissolved away as shown in Fig. 13.2.

Carbon dioxide in the steam can be decreased by removal of bicarbonate and carbonate alkalinity in the makeup water. This can be accomplished by a well-controlled lime softening program or by dealkalization, demineralization, reverse osmosis, or degasification processes. (A small amount may be lost by deaeration, depending on makeup water pH.) These processes are never 100% complete, so some bicarbonate/carbonate is always present in the makeup water, the actual amount depending on the pretreatment process. As a result, some CO_2 is always present in the steam.

Figure 13.2 Carbon dioxide corrosion.

Estimating the Amount of Carbon Dioxide in Steam

There is no accurate means of determining CO_2 in steam. Analytical field methods only detect free CO_2 (uncombined with amines or ammonia), and laboratory methods require fixing a sample and transporting it off-site for analysis. The sample is easily contaminated during both steps. Various equations have been developed for the estimation of CO_2. All of them generally estimate the correct range, although some might end up closer to the actual concentration than others.

Oxygen

Oxygen (O_2) is present in most makeup waters, but is usually reduced before entering the boiler by deaeration or chemical oxygen scavenging. If oxygen is not removed, it will flash from the boiler water and be carried along with the steam. This is probably the most critical source of oxygen in the condensate system. The oxygen flashed with the steam is present when condensation first occurs—the time when the metal is most susceptible to attack. Fortunately, large amounts of oxygen are easily kept from operating systems by mechanically deaerating the feedwater and then adding chemical oxygen scavengers.

The major source of condensate oxygen, however, is air inleakage into the system itself. Oxygen concentrations greater than 50 μg/L are typical of systems with air inleakage. The final concentration is largely dependent on the temperature of the condensate.

Oxygen can leak into a system via absorption into the condensate in atmospheric systems (vented receiver tanks), with raw water inleakage, and as air drawn in through small leaks, when the system is under a vacuum or operates intermittently and pulls a vacuum as the equipment cools (e.g., at threaded joints, heat exchangers, faulty steam traps, packing glands, and vented receivers). Severe pitting caused by oxygen attack can frequently be found at or just below the liquid surface in partially filled vessels and pipes, and at points above the surface where condensate droplets are formed. Although chemical solutions to this problem exist, air inleakage should be solved first by making the required system repairs.

Oxygen in condensate systems can cause severe pitting corrosion (Fig. 13.3). These oxygen pits can rapidly corrode through metal surfaces, greatly reducing equipment life and contaminating feedwater with undesirable corrosion products. Oxygen in the condensate reacts with iron to form ferric hydroxide:

$$4Fe + 6H_2O + 3O_2 \rightarrow 4Fe(OH)_3 \qquad (13.5)$$

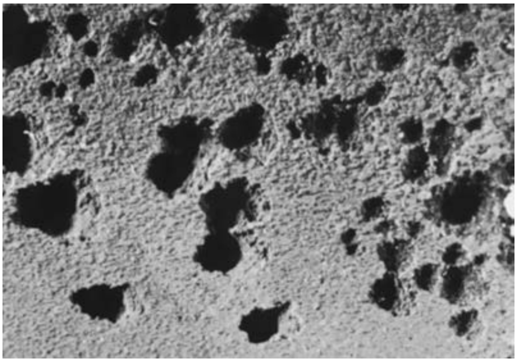

Figure 13.3 Oxygen pitting.

The ferric hydroxide then generally reverts in the condensate to form particulate iron oxide:

$$2\text{Fe(OH)}_3 \rightarrow \text{Fe}_2\text{O}_3 + 3\text{H}_2\text{O} \tag{13.6}$$

The iron oxide may further oxidize and is usually found in deposits on heat transfer surfaces as combinations of FeO, Fe_2O_3, and Fe_3O_4. These oxides often precipitate and settle in the condensate system in areas of low flow or reduced pressure. Deposits of this type have been known to build up to the point where condensate flow is severely restricted and even blocked.

When corrosion is controlled by the diffusion of oxygen, the corrosion rate at a given oxygen concentration approximately doubles for every 54°F (30°C) rise in temperature.

The corrosion rate in an open vessel where dissolved oxygen is allowed to escape, increases to about 176°F (80°C) and then falls to a very low value at the boiling point of water (Fig. 13.4).

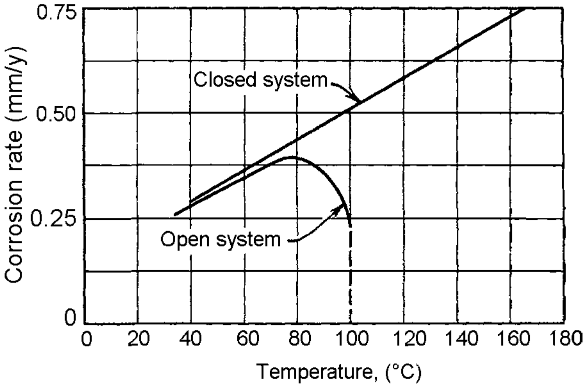

Figure 13.4 Effect of temperature on corrosion of iron in water containing dissolved oxygen (1 ipy = 1000 mpy = 25.4 mm/y).

The corrosion rate decrease above 176°F (80°C) is related to the significant decrease of oxygen solubility in water as the temperature approaches the boiling point. In a closed or unvented system, oxygen cannot escape, and the corrosion rate continues to increase with increasing temperature, until the corrosion process has consumed all oxygen.

At 140°F (60°C), oxygen is 6 to 10 times more corrosive to iron than the molar equivalent concentration of carbon dioxide. At pH levels below 6.0, corrosion of mild steel appears as a general metal loss with rough surfaces and some pitting present. At higher pH, the characteristic pitting attack is more noticeable.

Oxygen is also aggressive toward copper and its alloys. Oxygen can combine directly with copper to form cuprous or more often cupric oxide. Cupric oxide (CuO) is dark and provides a somewhat protective layer, preventing further attack. Cuprous oxide (Cu_2O) is red and indicates active corrosion.

In the presence of oxygen at pH above 9.2, any copper complexing agent such as ammonia can destroy the protective cupric oxide film, exposing fresh metal surface to further attack. Control of ammonia is the first line of defense against oxygen attack on copper.

Carbon Dioxide Plus Oxygen

The corrosion reaction of carbonic acid with iron is pH dependent, resulting in the evolution of hydrogen and the formation of ferrous bicarbonate. Experience has shown that when oxygen is present along with the carbon dioxide in the condensate, corrosion rates are greatly accelerated. In the presence of both carbon dioxide and oxygen, two cathodic reactions are now possible: evolution of hydrogen [Eq. (13.4)] and reduction of oxygen [Eqs. (13.7) and (13.8)], the latter being a faster reaction:

$$2Fe + O_2 + 4H^+ \rightarrow 2Fe^{+2} + 2H_2O \tag{13.7}$$

$$4Fe^{+2} + O_2 + 4H^+ \rightarrow 4Fe^{+3} + 2H_2O \tag{13.8}$$

The combination of carbon dioxide and oxygen appears to accelerate corrosion by 10 to 40% more than the corrosion rate occurring by either gas alone. Additionally, oxygen may react with existing corrosion products and further perpetuate the process by releasing CO_2. An example of this is shown by the following reaction:

$$4Fe(HCO_3)_2 + O_2 \rightarrow 2Fe_2O_3 + 4H_2O + 8CO_2\uparrow \tag{13.9}$$

The overall corrosion can be very severe and appear as worming or surface roughness, as shown in Fig. 13.5. At pH less than 6.0, corrosion is attributed mainly to the carbon dioxide content.

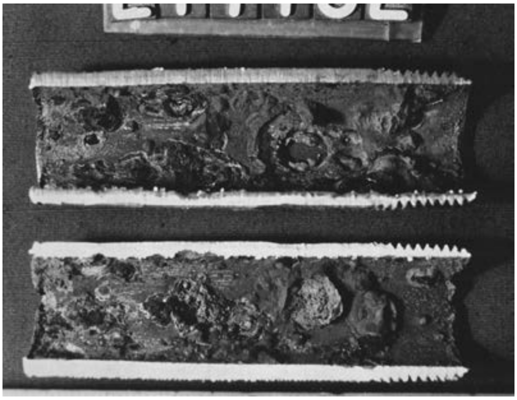

FIGURE 13.5 Internal surface of condensate line.

Where oxygen is also present, it acts to increase the rate of acidic attack. The type of oxygen pit developed is influenced by the condensate pH. Oxygen pitting begins at the weak points in the iron oxide film or at sites where it is damaged. At low pH, the iron oxide film is not very protective, so the pits tend to be large. As the condensate pH rises, the iron oxide film becomes more protective, and the pits tend to be smaller. In the pH range of 6 to 8, with oxygen concentrations between 0.5 and 4.0 mg/L, the rate of general attack is proportional to the oxygen concentration.

Ammonia

Ammonia enters the boiler system in a number of ways. It is present in some natural waters as the result of breakdown of organic materials. A greater number of city and municipal water departments are now using ammonia to stabilize chlorine as chloramine in order to obtain better biological control in the drinking water distribution system. Chloramines that pass through pretreatment systems and enter boiler feedwater generate ammonia. Another source of ammonia is chemical breakdown of boiler water additives such as hydrazine or hydrazine alternatives (e.g., carbohydrazide, diethylhydroxylamine, and methylethylketoxime), some polymers (e.g., acrylamide-based polymers), and amines [generally at temperatures above 850°F (454°C)]. Ammonia can also result from process contamination or intentional feed as condensate treatment.

Ammonia can reduce the corrosion of ferrous metals by neutralizing carbonic acid and raising the pH of the condensate. However, ammonia is corrosive to copper alloys in the presence of oxygen. The oxygen reacts with the copper to produce a copper oxide coating on the metal, which is rapidly dissolved by ammonia.

Dissolved Oxygen, μg/L	**Maximum Allowable Ammonia, mg/L**
0–20	0.5
21–50	0.3
Over 50	Any level may cause a problem

Table 13.1 Relationship of Oxygen and Ammonia

This oxidation and dissolving reaction produces a soluble cupric-ammonia complex:

$$Cu + \tfrac{1}{2}O_2 \rightarrow CuO \tag{13.10}$$

$$CuO + 4NH_3 + H_2O \rightarrow Cu(NH_3)_4^{+2} + 2OH^- \tag{13.11}$$

This rapid creation and destruction of the copper oxide film results in a very destructive cycle, which is especially aggressive below pH 8.5 and above pH 9.2.

Table 13.1 shows the concentrations of ammonia and oxygen that can typically be tolerated in minimizing copper corrosion.

The main sources of ammonia present in a condensate system should be located and reduced or eliminated. Concentrations can sometimes be lowered by periodically discarding the aftercooler drips from the condenser steam jet air ejector. Ammonia is usually highly concentrated in these drains.

In systems with mixed metallurgy or insufficient sample points, a filming amine or Nalco ACT® provide protection against ammonia, if the proper pH range is maintained.

Sulfur Dioxide and Hydrogen Sulfide

Catalyzed sodium sulfite (Na_2SO_3) is commonly used to scavenge dissolved oxygen from boiler feedwater following deaeration. While this treatment provides excellent oxygen removal, it has certain limitations, including a recommended boiler drum pressure limitation of 900 psig (6.2 MPag). Sodium sulfite begins to decompose at approximately 600 psig (4.1 MPag) to form sulfur dioxide (SO_2) and hydrogen sulfide (H_2S) gases, which are carried with the steam. The rate of decomposition increases rapidly above 900 psig (6.2 MPag):

$$Na_2SO_3 + H_2O \rightarrow SO_2\uparrow + 2NaOH \tag{13.12}$$

$$4Na_2SO_3 + 2H_2O \rightarrow 3Na_2SO_4 + 2NaOH + H_2S\uparrow \tag{13.13}$$

These gases dissolve in the condensate much in the same way as CO_2. However, the sulfurous acid (H_2SO_3) produced by SO_2 is considerably stronger than the carbonic acid produced by CO_2. Correspondingly, the acid neutralization becomes more difficult, and the corrosion process proceeds faster. Sulfur, sulfides, and H_2S are particularly corrosive to copper and its alloys. There is also indication that the presence of H_2S and SO_2 in the steam can cause stress corrosion cracking of copper and its alloys, especially in steam turbine condensers.

Process Contamination and Organic Acids

Aside from the various gases that can dissolve in the condensate from thermal breakdown or inleakage, condensate can become corrosive through process contamination. Because of the natural high purity of condensate, very small amounts of contaminant can render it extremely corrosive and unsuitable as feedwater. Process liquids, catalysts, cleaners, solvents, equipment and fabrication oils and lubricants, and condenser cooling water are all potential contaminants.

Process contaminants may be corrosive in their original state, or they may decompose to corrosive compounds in the boiler. Decomposition of organic molecules in the boiler water generally results in the formation of low molecular weight organic acids (e.g., acetic, formic, and glycolic acids) and carbon dioxide. These low molecular weight organic acids are volatile, although their volatility is relatively low compared to commonly used neutralizing amines. All are considerably stronger than carbonic acid and increase the amine demand in the condensate. They also consume alkalinity in the boiler water.

Another concern is contamination originating in jacketed reaction vessels. Reactors, mix tanks, blend tanks, and other reaction vessels are often surrounded by jackets or coils that can heat or cool the vessel and its contents during processing. This jacketed vessel, sometimes called an annular space heat exchanger, is typically an open space surrounding the vessel through which steam, cooling water, and other fluids flow. Condensate from these vessels is frequently contaminated by cooling water. Precautions should be taken to isolate reaction vessels in order to prevent contaminated condensate from returning to the boiler system.

Methods of Condensate Corrosion Inhibition

Effective corrosion control for a condensate system must include mechanical, operational, and chemical (MOC) aspects. Chemicals alone are not adequate or cost-effective.

Mechanically, the elimination of all avenues of air, water, and process inleakage is an essential part of system protection. Feedwater oxygen can be almost completely eliminated by mechanical deaeration plus the use of an oxygen scavenger. In addition, various pretreatment processes such as hot lime softening, dealkalization, demineralization, and reverse osmosis can be used to reduce makeup water bicarbonates and carbonates.

All equipment must be properly operated and maintained to achieve the desired results. Maximum condensate recovery for boiler feedwater reduces potential CO_2 generation and subsequent amine consumption and condensate corrosion. Good monitoring of pretreatment, feedwater, and condensate systems coupled with rapid response to upsets is essential for effective corrosion control.

However, even with excellent pretreatment and feedwater deaeration, chemical inhibitors are still necessary for complete protection. Chemically, four types of inhibitors are used for condensate corrosion control: neutralizing amines, filming amines, nonvolatile filming technology, and oxygen scavengers/metal passivators.

Neutralizing Amines

Neutralizing amines are volatile, alkaline compounds that are added to either the boiler feedwater or the steam supply systems. They function by volatilizing into the steam and redissolving in the condensate with the CO_2. The amines chemically neutralize carbonic acid, or any other acid, present in the system. They raise pH to a level at which the condensate is much less aggressive to the system metal.

Most commercially available neutralizing amine condensate treatments are blends of various amines. The blends offer combinations of certain characteristics that are unique to each amine. The characteristics of greatest importance when selecting amines are specific volatility (*V*/*L* ratio), basicity, acid neutralizing ability, thermal stability, and compliance with government regulations. Amine recycle may also be important. Each characteristic must be considered when selecting a condensate corrosion inhibitor program.

Volatility

Every gas in a condensate system has a specific volatility or vapor to liquid distribution ratio (*V*/*L*). The *V*/*L* distribution ratio is defined by:

$$\frac{V}{L} = \frac{V_{\text{conc}}}{L_{\text{conc}}} \tag{13.14}$$

where V_{conc} = concentration in the vapor or steam phase
L_{conc} = concentration in the liquid or condensate phase

The *V*/*L* distribution ratio indicates how much of the species will condense with the condensate or stay with the steam. For example, a *V*/*L* ratio of 4.0 indicates that 4.0 mg/L of amine must be present in the steam to get 1.0 mg/L in the condensate (5 mg/L total amine present). The higher the *V/L* ratio, the more amine will be present in the steam for each mg/L present in the liquid. The *V/L* ratio is applied at each point of condensation. To neutralize carbon dioxide, the amine must be present in the condensate as the CO_2 dissolves.

V/L ratios vary with pressure, temperature, pH, and other operating conditions. They do not depend on distance from a steam generator or boiler. Table 13.2 shows how the *V/L* ratio of three common neutralizing amines and carbon dioxide vary by pH. Table 13.3 shows how the *V/L* ratios of various amines vary by pressure for the pH range 7.5 to 9.5.

V/L distribution ratios are significant only when a phase separation occurs. For example, in a flash tank, condensate enters the vessel, but both condensate and steam exit the vessel. Low volatility amines such as morpholine tend to be present in greater concentration in the condensate exiting the flash tank. If morpholine alone were fed to the system, the condensate exiting the flash tank might have adequate protection, but the flashed steam could have a low pH when finally condensed. High volatility cyclohexylamine tends to be present at higher concentrations in the steam exiting the flash tank. If cyclohexylamine alone were fed to the system, the condensate exiting the flash tank would likely have adequate protection, whereas the flashed

	Cyclohexylamine		**Diethylaminoethanol**		**Morpholine**		**Carbon Dioxide**
Pressure psig (kPag)	**pH 7.5–9.5**	**pH 10–11.5**	**pH 7.5–9.5**	**pH 10–11.5**	**pH 7.5–9.5**	**pH 10–11.5**	**pH 7.5–9.5**
10 (69)	2.7	13	2.2	4.1	0.4	0.4	3.0
150 (1034)	4.0	20	4.3	5.8	0.5	0.99	8.5

Table 13.2 *V/L* Ratios for Carbon Dioxide, Cyclohexylamine, Diethylaminoethanol, and Morpholine

	Pressure, psig (kPag)				
Amine	**10 (69)**	**50 (345)**	**150 (1034)**	**600 (4137)**	**900 (6205)**
Ammonia	3.0	6.7	7.0	5.0	4.3
Carbon dioxide	3.0	4.8	8.5*	15.8	99
Cyclohexylamine	2.7	3.0	4.0	10	6.6
Diethylaminoethanol	2.2	3.0	4.3	5.2	4.5
Morpholine	0.4	0.44	0.5	1.22	1.22

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*At 350 psig (2413 kPag)

Table 13.3 *V/L* Ratios of Various Neutralizing Amines Used in Boiler Systems (pH 7.5–9.5) steam would have a higher pH (than with morpholine) at final condensation. This example illustrates the necessity of amine blends for adequate corrosion protection of the entire condensate system.

Any vented process unit or condensate receiver tank has a phase separation (release of some steam, CO_2, amines, and NH_3). A sample of condensate exiting a vented unit is often not representative of the condensate entering it. pH readings taken from these locations will typically be higher than the pH of the condensate entering the receiver, due to the loss of more CO_2 than amine or ammonia.

V/L ratios are not significant when total condensation occurs. In units with total condensation, all the carbon dioxide, amines, and ammonia in the steam entering a unit are dissolved into the condensate (no phase separation exists).

Basicity

Basicity is a measure of amine hydrolysis. Neutralizing amines used for condensate treatment are primary, secondary, or tertiary amines and can be represented by the general formula RNH_2, where R denotes an organic radical. Hydrolysis generates a captive hydroxide ion (OH^-), which is present in solution as long as the amine molecule is present [Eq. (13.15)]. In the neutralization process, the hydrolyzed amine reacts with the bicarbonate to form an amine bicarbonate salt [Eq. (13.16)]. Equation (13.3) is repeated here so that the full reaction can be seen. The OH^- group generated by amine hydrolysis reacts with the H^+ group from carbonic acid to form water [Eq. (13.16)].

$$RNH_2 + H_2O \rightleftharpoons RNH_3^+ + OH^- \tag{13.15}$$

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \tag{13.3}$$

$$RNH_3^+ + OH^- + H^+ + HCO_3^- \rightleftharpoons RNH_3HCO_3 + H_2O \tag{13.16}$$

The basicity of neutralizing amines varies. For example, cyclohexylamine is a much stronger base than morpholine. Table 13.4 shows basicity constants for various amines. Past a certain pH, additional quantities of the weaker neutralizing amines such as morpholine do little to further increase pH.

Amine	Molecular Weight	pKa
Ammonia	17	9.3
Cyclohexylamine	99	10.6
Diethylaminoethanol	117	9.6
Morpholine	87	8.4

Table 13.4 Basicity Constants and Molecular Weight for Common Neutralizing Amines

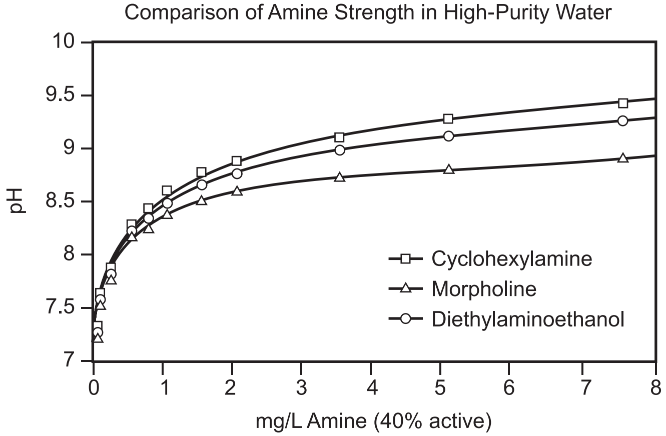

Figure 13.6 pH effect of acid neutralizing ability and basicity of common neutralizing amines.

Acid Neutralizing Ability

Another very important aspect of amine selection is its acid neutralizing ability. This is the amount of amine required on a weight basis to neutralize one mole (44 g) of carbonic acid. This characteristic is dependent upon the equivalent weight of the amine. The net reaction shown by Eq. (13.16) goes to exhaustion of either amine or acid. The final pH is then determined by hydrolysis of the left over component. On a mass basis, lower molecular weight amines neutralize more carbonic acid than higher molecular weight amines.

Figure 13.6 shows a graphic representation of the combined effects of acid neutralizing ability and basicity.

Thermal Stability

All organic molecules, including amines, have specific temperature limitations, above which they thermally decompose. Most water treatment chemicals commonly used in boiler systems have been chosen for their exceptional thermal stability, yet all eventually break down in the boiler system given sufficient heat and holding time.

Amine thermal stability is primarily dependent on time at temperature, but system oxygen can also be a factor. The superheater is typically the location of highest heat within the boiler system. Because exposure time to superheat temperatures is extremely short, many amines can be used at temperatures above their known decomposition temperatures without appreciable loss. Amines used in systems with reheat have significantly more exposure time at high temperatures and typically see a higher percentage loss.

Amine	Approximate Temperature Limit, °F (°C)
Ammonia	No limit
Cyclohexylamine	1100 (593°C)
Diethylaminoethanol	850 (454°C)
Morpholine	1100 (593°C)

Table 13.5 Recommended Temperature Limitations for Neutralizing Amines

In work reported by the Electric Power Research Institute (EPRI) in the early 1990s, the relative stability of several amines was listed as:

Monoethanolamine > methoxypropylamine > morpholine

Table 13.5 shows suggested temperature limitations for some of the neutralizing amines commonly used.

Thermal degradation of the neutralizing amines typically results in the generation of lower molecular weight amines and organic acids, as well as ammonia. For example, the decomposition of morpholine is well known and is shown in Fig. 13.7. The organic acids

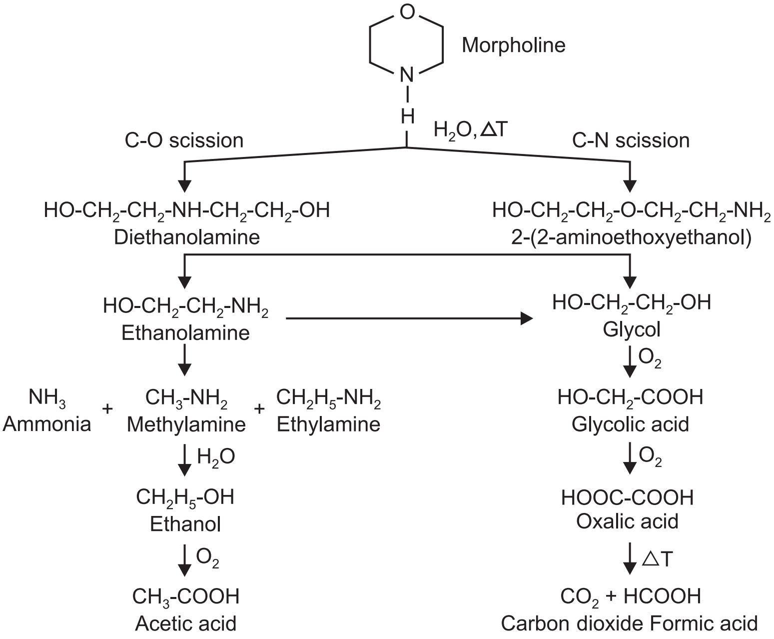

Figure 13.7 Decomposition of morpholine.

can cause various problems: cation conductivity is elevated, pH can be depressed in some areas, and condensate polisher (anion) loading is increased. In addition, the original amine is destroyed, and the amines formed are typically more volatile. Thus, the volatility blend provided by the original program is changed, and portions of the condensate system may not be as well protected.

In high-pressure power plants, the benefits of feeding neutralizing amines must always be weighed against potential problems caused by increased total organic carbon (TOC) and cation conductivity.

Amine Recycle

Much of the neutralizing amine fed to a boiler system is recycled. The total amine present in a boiler system is a combination of the amount of amine returned with the condensate, plus the existing amine feed rate. Feed rates can be reduced substantially by returning higher amounts of condensate.

Losses include:

- Sewered or lost condensate—all amine present is lost with the condensate.
- Vented returns—primarily the more volatile amines (cyclohexylamine). A larger portion of CO_2 is generally lost than amine.
- Condensate polisher—depends on regeneration practices. Condensate polishers are capable of removing neutralizing amines, but many are run past the amine breakpoint. In addition, condensate polishers regenerated in the amine form will not remove amines.
- Deaerator venting—limited due to low mass flow rate and feedwater pH. The pH must be equal to or greater than the amine pKa for appreciable loss to occur.
- Boiler blowdown—depends on amine and blowdown rate. Loss of amines with low *V/L* ratios is greater than those with high *V/L* ratios. Mass loss is greater at low cycles than at higher cycles.

The total amine present in a boiler system is a combination of the amount of amine returned with the condensate (recycled) plus the fresh amine feed rate. Product feed rates can be reduced substantially by returning higher amounts of condensate.

Dosage Requirements

Neutralizing amine programs are generally effective when fed to maintain a condensate pH of 8.5 to 9.2 in systems with soft water makeup or 9.0 to 9.6 in systems with demineralized makeup. In systems containing copper alloys, a range of 8.8 to 9.2 provides optimum corrosion protection for both ferrous and copper alloyed portions of the system. Because the amines are added to the system in direct proportion to the amount of CO_2 in the steam, high-alkalinity feedwater requires considerable amounts of amine to obtain the desired pH range. The cost of such a program may be prohibitive, and alternative means of corrosion protection should be sought. Common pretreatment alternatives of the makeup water that reduce amine dosage requirements include dealkalization, demineralization, and reverse osmosis (RO).

Neutralizing amines themselves offer no protection from oxygen corrosion. Because they do elevate the pH, however, they can provide some indirect inhibition to oxygen attack, if the pH is raised to 9.5 or higher. If air inleakage is a problem in a system, an alternative must be considered. The use of filming materials in combination with neutralizing amines may be the cost-effective alternative needed for high-alkalinity systems or systems plagued by air inleakage.

Government Regulations

There are a great number of government regulations that govern the use of amines in steam. Two of the more commonly regulated areas are food contact and airborne concentrations. The regulations discussed here are for the United States. Different regulations of similar nature may apply in other countries.

In the processing of food, substances contacting the food (including any substance intended for use in producing, manufacturing, packing, processing, preparing, treating, packaging, transporting, or holding food) have the potential to become part of the food. As such, they are regulated by the U.S. Food and Drug Administration (FDA). Boiler water additives used in the generation of steam fall into this category. Under FDA regulations, only certain neutralizing amines can be used in the treatment of steam and condensate systems. In addition, their concentrations must remain below the specified limitations summarized in Table 13.6.

Boiler water additives used in the generation of steam for federally inspected meat or poultry, shell egg grading, or rabbit and egg processing facilities had historically been governed by the U.S. Department of Agriculture (USDA). In 2000, the National Sanitation Foundation (NSF) assumed previous USDA evaluation and registration responsibilities in this area. Approval by NSF should be listed on any product's Safety Data Sheet (SDS). USDA/NSF approval is by product and not by product component.

Often, steam from boilers is used to humidify building air, especially during the winter. When steam is introduced into the air, any volatile compounds contained in the steam are also introduced into the air. The American Conference of Governmental Industrial Hygienists (ACGIH) and the U.S. Occupational Safety and Health

Substances	Limitations
Cyclohexylamine	Not to exceed 10 mg/L in steam, and excluding use of such steam in contact with milk and milk products
Diethylaminoethanol	Not to exceed 15 mg/L in steam, and excluding use of such steam in contact with milk and milk products
Morpholine	Not to exceed 10 mg/L in steam, and excluding use of such steam in contact with milk and milk products
Octadecylamine	Not to exceed 3 mg/L in steam, and excluding use of such steam in contact with milk and milk products
The combined total of all amine concentrations must remain below 25 mg/L total actives.	

Source: 21 CFR 173.310(d) Boiler Water Additives.

Table 13.6 U.S. FDA Regulations for Amines

Administration (OSHA) are the two regulating bodies for airborne substances in the United States.

ACGIH has adopted standard threshold limit values—time weighted averages (TLV-TWA) for amines in air, based on their irritative properties. The TLV-TWA is the time-weighted average concentration to which nearly all workers may be exposed for eight hours per day, forty hours per week, without adverse effect. OSHA has established time-weighted average permissible exposure limits (PEL) for commonly used amines. These limits and odor threshold values are listed in Table 13.7. To date, no major agency or association has prohibited the use of steam treated with chemical additives for humidification, but questions and concerns about such use are common.

Amine	ACGIH TLV-TWA mg/L	OSHA PEL-TWA mg/L	Odor Threshold mg/L
Morpholine	20	20	0.14
Diethylaminoethanol	2	10	0.04
Cyclohexylamine	10	10	0.90

Table 13.7 Neutralizing Amine TLV, PEL, and Odor Threshold Summary

Filming Amines

Filming amines are high molecular weight amines consisting of very long-chain hydrocarbons. One end of the molecule is hydrophilic (attracts water), and the other is hydrophobic (repels water). The hydrophilic end physically attaches itself to the metal surfaces of the condensate system. As the density of the molecules on the metal surfaces increases, the hydrophilic ends create a monomolecular, nonwettable film on all metal surfaces that come in contact with the condensate. This film acts as a physical barrier between the metal surfaces and corrosive condensate, offering protection against both carbon dioxide and oxygen attack (Fig. 13.8).

Unlike neutralizing programs, filming amine programs do not neutralize CO_2. Therefore, their feed rates are not directly proportional to the amount of contaminant (O_2, CO_2, NH_3, etc.) in the steam. The amount of filming amine required is related to the system's surface area. This fact makes a filming amine program desirable in systems with high-alkalinity feedwaters or in areas of air inleakage, where a neutralizing program would be either cost-prohibitive or ineffective.

The protective amine film is generally quite stable, but high pH conditions may cause it to strip off the metal (pH above 8.0 for octadecylamine), while low pH (below 6.5) impairs the film

FIGURE 13.8 Condensate pipe treated with filming amine repels water.

adsorption on metal. Supplemental neutralizing amines or combination neutralizer/filmer programs are often necessary to maintain the correct pH control range. Filming amines can be worn or eroded away by the flow of water across the metal surface. They must be fed continuously to assure that no gaps in protection occur in any parts of the system.

Caution must be exercised when a filming amine program is started. Filming amines tend to clean up any iron oxide, scale, or contaminant on the piping while attaching to the metal. This may initially result in higher levels of solids in the condensate. In addition, excessive feed may cause the filming amine to accumulate as sticky masses (gunk balls) in receivers, steam traps, valves, or any collection point. Periodic testing is required to maintain a specified residual of filmer in the condensate to avoid such deposits. A filming amine program should start with a low dosage, which is gradually increased until residual limits are met.

Oxygen Scavengers/Metal Passivators

Volatile oxygen scavengers can be used in combination with neutralizing amines. The scavenger reacts directly with oxygen present in the condensate, while the neutralizing amine provides protection from CO_2 corrosion. Volatile oxygen scavengers may also enhance or accelerate metal passivation, but their ability to do this varies greatly. At condensate temperatures, metal passivation may preferentially occur over oxygen scavenging. Oxygen corrosion inhibitors do not provide protection against carbon dioxide or ammonia. Carbonic acid attacks the passive magnetite film, so passivation improves greatly above pH 8.3, where this acid is not present. Most of these chemicals are a potential source of ammonia.

Sulfite is not acceptable in condensate systems, because it adds solids to the condensate and is not volatile. Erythorbate is not volatile but can be used in condensate systems, if fed into the condensate. It should not be fed directly to the steam. Hydrazine, carbohydrazide, and diethylhydroxylamine are oxygen corrosion inhibitors that can be fed directly to the steam. Carbohydrazide reacts with oxygen both directly and through the generation of hydrazine. A pH of 8.5 must be maintained to promote a passive metal surface. Filming amines are usually more cost-effective than oxygen corrosion inhibitors.

Minimizing the Effect of Contaminated Condensate

Steam condensate is usually recycled because the condensate is a valuable product and its reuse is considered essential to the economics of steam and power production. Although impurities in condensate are usually quite low, in some instances they must be removed before the condensate can be reused, or the condensate must be discarded. These impurities originate from dissolved solids introduced through condenser leaks, dissolved solids carried over with the steam from the boiler water, metallic species originating from condensate equipment corrosion, and various process contamination events.

Condensate polishers can be used to improve the purity of condensate. The primary purpose of condensate polishers is to filter corrosion products such as iron and copper oxides (crud). They also remove traces of soluble salts, resulting from condenser leakage and carryover.

Another means of minimizing the effect of contaminated condensate is to discard it before it reaches the polishers. Depending on the degree of contamination, this is often a prudent action. Badly contaminated condensate may quickly exhaust or foul polishers, allowing the full amount of contamination to return to the feedwater system.

Automatic diversion systems can be used to detect and discard condensate that is unfit for reuse. These systems must be installed properly to be effective. Velocities of pumped condensate returns are commonly 6 to 8 ft/s (1.8–2.4 m/s). Automatic control valves can take 4 to 5 seconds to actuate, close, and divert the condensate to sewer. This means there must be a minimum of 24 to 40 ft (7.3–12 m) between the detection device and the valve, if all contamination is to be prevented.

Most detection devices require additional response time, since they often need a cooled sample and are not located immediately on the return condensate line. Sample line size (diameter and wall thickness), length, and volume determine how much additional response time this adds. Additional time is required for the contaminant to rise to the alarm concentration. There may also be a lag time inherent in the method of analysis or detection device that must be added to the total response time. Each of these factors increases the distance required between the detection device (or sample tap) and the automatic dump valve.

The required distance quickly becomes excessive, and a failure of either the valve or the detection device allows contamination back into the boiler system. Industrial plants with potentially troublesome condensate have learned that it is much more reliable to install a redundant automatic diversion system than to rely on a single system and try to get sufficient distance between the sample tap and valve. The first automatic diversion valve and detector should be close to the point of potential contamination. The second system can be just before the final condensate collection tank and monitor combined return streams. Be sure to consider the amount of condensate dumping that can be tolerated. This is generally considered to be the amount of extra makeup that the pretreatment can supply.

If the contaminant is cationic or anionic in nature, it may be detectable by simply monitoring specific or cation conductivity. Many particulates, suspended solids, and organics are nonionic, however, and do not affect conductivity values. In those plants, an in-line TOC monitor may be used to detect organic condensate contamination. Turbidimeters, particle counters, fluorometers, and chromatographs have had some success in detecting certain nonionic organic contamination. Turbidimeters and particle counters are most commonly used to detect particulates or suspended solids such as particulate iron.

Valves should be exercised and meters calibrated to assure they are working properly. Meter measurements should be verified by grab sample at a frequency that assures the protection and reliability of the boiler system. The required frequency depends on the reliability of the meter, frequency of condensate contamination, and the effect of the contaminant on the boiler system, but should typically be done at least once per week.

System Design and Maintenance

Steam condensate system design and maintenance not only affect the delivery of steam, but also the ability to remove condensate from the system and the potential for system corrosion. Poor drainage of condensate can result in corrosion, erosion, and water hammer, all of which eventually result in leaks and failures and limit the amount of condensate returned for reuse as boiler feedwater.

It is not within the scope of this chapter to thoroughly discuss all the design issues that might affect a plant's ability to return condensate. However, common good engineering practices are listed below:

- Supply dry, high-quality steam. Steam quality must generally match process requirements and be of sufficient quality (dryness) not to erode system components. In those instances when high-moisture steam is used, a steam separator should be considered. Supply lines should be insulated and trapped to prevent accumulation of condensate.
- Isolate steam from unused lines with properly located isolation valves. Any dead leg open to steam should be trapped to prevent condensate accumulation.
- Make sure lines and traps are properly sized. This minimizes pressure loss, erosion, heat loss, and blow-through steam. Horizontal lines should be sloped at 1 inch per 10 feet (8.3 mm/m) in the direction of flow and properly supported to prevent sagging and condensate accumulation.
- Install sufficient traps on steam mains to remove condensate as quickly as possible. At a minimum, traps should be located

on all vertical risers, upstream of control valves, and at 100 to 300 ft (30–91 m) intervals along horizontal runs of pipe.

- Use the correct trap for the application. Never group trap (using one trap on multiple lines). Group trapping invariably leads to back-up of condensate in the system.
- Ensure that piping allows the condensate to be removed effectively. Coils should be fitted with vacuum breakers to allow condensate to drain freely. Waterlogged equipment not only fails to operate as expected, but is also prone to corrosion and water hammer.
- When possible, avoid any increase in elevation on return condensate lines. Condensate that is evacuated to a higher elevation does not flow by gravity. It requires a pressure slightly greater than the head pressure resulting from the elevation rise. When elevation of condensate after a trap is necessary, a pumping trap may be necessary to assure good drainage.
- Install receiver vents of the proper size. Receiver vent lines that are too small restrict the loss of flash steam. This in turn results in hotter condensate return temperatures and potential problems with cavitation of electric condensate return pumps. Alternatively, use pressure-powered pumps.
- Make sure condensate return lines are sized to move the flash and blow-through steam present after a trap, as well as the condensate. Steam (vapor) is more voluminous than condensate (liquid). Condensate piping that is sized for only liquid is grossly undersized.
- Choose materials of construction that minimize corrosion.
- Inspect and repair steam traps. Steam traps can be a source of significant energy loss (steam and condensate). Implement routine steam trap maintenance programs for regular inspection, testing, and repair of failed traps. In most systems, there is opportunity for significant savings and near immediate payback on the minimal investment required to inspect and repair steam traps.

Evaluating Results

Effective monitoring and control of the steam condensate system is necessary to assure proper corrosion protection. Contamination originating in the condensate system can easily affect the entire boiler system. Without adequate monitoring and control, the system will most likely suffer increased operational costs and unscheduled outages.

The American Society of Mechanical Engineers (ASME) provides excellent recommendations for sampling from boiler systems in their document "Consensus on Operating Practices for the Sampling and Monitoring of Feedwater and Boiler Water Chemistry in Modern Industrial Boilers" (CRTD-Volume 81). The American Society for Testing and Materials (ASTM) has also written numerous documents that cover the practice of sampling boiler system streams.

Successful monitoring and control requires that representative samples be obtained at multiple locations throughout the system. Typically, samples that exceed 100°F (38°C) must be cooled before collection to maintain a representative sample and assure the safety of personnel. Temperature should ideally be maintained at 70 to 90°F (21–32°C), with 77°F (25°C) preferred, to prevent significant loss of volatile gases such as CO_2 and O_2. The sample may be throttled at the outlet but not at the inlet. This is done to prevent a vacuum from occurring in the coil and drawing in air, which can yield false results.

Samples must be taken from a location that is representative of the system. Dead legs or end-of-the-line locations may be convenient, but are seldom representative. If chemicals are injected or other streams introduced into the line to be sampled, the collection point must be placed far enough downstream to ensure a mixed sample. With turbulent flow (Reynolds number > 4000), a tap location 25 pipe diameters downstream is considered acceptable. With laminar flow, a length equivalent to 50 pipe diameters is recommended (ASTM D 3370-95a).

The contaminant typically present in condensate is particulate iron. Particulate iron is not conductive and will not be detected by a conductivity probe. As a particulate, it tends to drop out of the bulk water behind fittings and valves, within wide spots in the line, or wherever velocity is insufficient to keep the particle entrained in the liquid. A long vertical rise typically causes a problem with maintaining particulate iron in the sample (gravity works against the particle remaining in the bulk water).

Why Treat Condensate?

The industry practice of treating condensate exists because it is usually more cost-effective to treat condensate than to live with the results of corrosion. Even plants that do not return any condensate can save many of the costs listed below through condensate treatment.

Condensate corrosion results in many additional plant costs:

- Increased fuel consumption due to steam and condensate leaks throughout the steam and condensate systems
- Replacement costs for equipment, heat exchangers, lines, tanks, steam traps, etc.

- Increased maintenance costs
- Unscheduled outages and loss of equipment use that lead to production losses
- Equipment fouling, which can affect product quality if design conditions cannot be maintained
- Dirty condensate
    - Can result in dirty boilers, increased fuel consumption, reduced boiler reliability, and boiler failures
    - May require sewering because it is unfit for reuse as boiler feedwater
    - May require clean up (e.g., filtration or polishing), incurring additional costs for reuse

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SECTION 3.3

Applications—Cooling Water Systems

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CHAPTER 14

Cooling System Dynamics

Mechanical-Operational-Chemical Survey Concepts

A complete mechanical-operational-chemical (MOC) survey provides mechanical details about the process and cooling system, collects operating history data, evaluates costs of operation, and details the chemistry of the system. Every cooling water system presents a unique combination of equipment, operating controls and history, water chemistry, and contaminants. The goal of the survey is to understand the interactions between the mechanical, operational, and chemical aspects of the entire system.

Data collected in the survey should be compared to design specifications to evaluate current operation versus initial design. Differences can help point to opportunities for improvements, areas of stress in the system, or problems that need to be solved. System stress can be defined as any mechanical, operational, or chemical factor that negatively impacts system performance. Examples of system stress include high surface temperature in heat exchangers, low flow rate, high concentration ratio, or poor control of tower operating parameters. Exceeding any of these stress points can cause corrosion or fouling of the system. Responses to reduce or control system stress include adjustments to the chemical treatment program, concentration ratio adjustment, or mechanical improvements to the system. Optimizing the treatment program for the system stress points will provide the optimum results and the best value for that system. The chapter on cooling water treatment (Chap. 19) will cover cooling water system stress and the proper responses to different stresses in more detail.

Survey Data Analysis

Analysis of the information collected can identify stresses in a cooling system, like scale in a high-temperature, low-flow heat exchanger or corrosion problems due to control parameter variability. These stresses on a cooling system are very system specific. Using these data, a program can be designed to manage the system at the optimum points for stress and lowest cost. The goal is to be able to maintain a reasonable level of stress in the system at the lowest operating cost. Assessment of the impact of various stresses involves understanding the costs of different treatment program operating modes. Consequently, to be able to demonstrate the value of stress management, identification of the stresses with greatest impact on cooling water system performance is essential.

Modeling the water chemistry under different conditions is a valuable method to determine the scaling potential of the system. Computer modeling programs can evaluate potential mineral scale formation, corrosion tendencies, and treatment programs under a wide range of cooling water system conditions. Computer modeling programs can be used for thorough analysis of stresses due to water chemistry and control variability. These programs can quickly indicate conditions that may cause problems at various concentration ratios, pH, or contaminant levels. This can show the correct operating conditions to optimize system operation at optimum stress levels. The impact of poor control is poor results, and each control parameter may have a different effect on the system (Fig. 14.1). Often, system control is the most important element for successful operation of a cooling water system.

The next step is to understand the extent to which these key stresses affect the total cost of operation (TCO) as shown in Fig. 14.2. By understanding the total costs of the cooling water system operation and treatment, the best return on investment (ROI), and best environmental return on investment (e^{ROI}) can be achieved. The MOC concepts provide a complete framework to gather and analyze the information needed to reach the optimum TCO and the best ROI

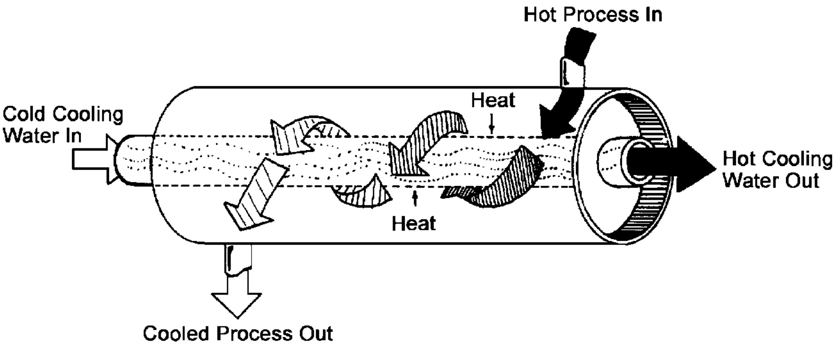


FIGURE 14.1 Heat flows from the hot process to the colder cooling water in this simple example of a heat exchanger.

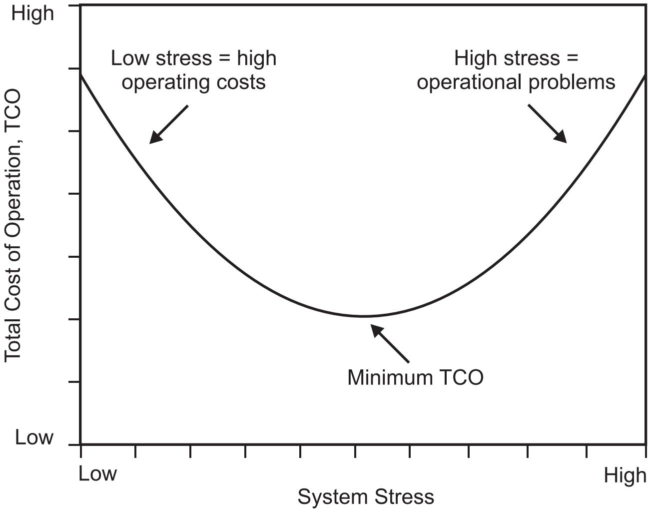


Figure 14.2 Optimum TCO is a balance between stresses that are too high and too low.

from an optimized program. This chapter illustrates the key parts of an MOC survey: heat transfer and heat exchangers, cooling water system types, and system dynamics calculations.

Heat Transfer

Heat transfer is the science that deals with the exchange of heat between hot and cold bodies. By definition, heat passes from the warmer medium to the cooler one. In typical industrial applications, the product or process being cooled is the heat source and cooling water is the receiver. Cooling water usually does not contact the heat source directly. The process fluid or gas to be cooled is usually separated from the cooling water by a barrier that is a good conductor of heat, usually a metal. The barrier that allows heat to pass from the source to the receiver is called the heat transfer surface, and the assembly of barriers in a containment vessel is a heat exchanger. A heat exchanger is a device for transferring thermal energy from one medium to another, as for example, between two liquids or between a gas and a liquid. Generally, an exchanger consists of two sections, one for each medium.

There are three distinct ways in which heat may pass from a source to a receiver, although most engineering applications are combinations of two of the methods. These are conduction, convection, and radiation. Conduction is how metal transfers heat from one part of the metal to another part. The metal components of the heat

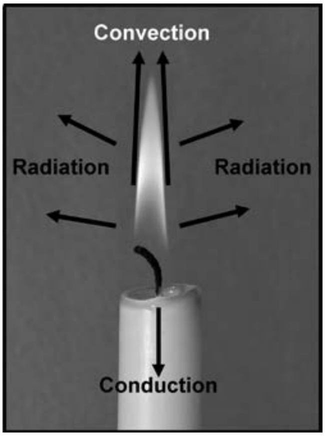


FIGURE 14.3 Illustration of the three processes of heat transfer.

exchanger carry heat away from the process fluid by conduction. Convection is primarily how fluids (liquids and gases) transfer heat within the fluid itself. Rapid water flow is very important in heat exchangers, because water turbulence assists the convection process in distributing the heat throughout the water. Finally, radiation is the transfer of heat in the form of energy rays or waves, like infrared energy. Light from the sun heats the earth by radiation. Similarly, the return water piping of a cooling system will lose some heat by radiation to the surrounding atmosphere.

Figure 14.3 illustrates the three methods of heat transfer with a burning candle. The hot gases from the flame carry heat into the air by convection. The convection currents in the air can be seen by the distortion of view when looking through the air above the candle. Heat radiation is felt by placing a hand near the side of the flame. The hot wax under the flame carries the heat into the candle by conduction through the wax.

Heat Exchangers

The most common of all heat exchangers is known as the shell-and-tube exchanger. In this exchanger, one medium flows through a bundle of tubes, while the second medium passes around this bundle inside the exchanger shell, as shown in Fig. 14.4. No matter what the configuration, the exchanger must be arranged so that the maximum amount of surface exists between the fluids exchanging heat. This can be achieved by running one fluid back and forth in two or more "passes" on the tube side (the water makes two passes in the exchanger in Fig. 14.4), while the other fluid flows across the outside of the tubes around baffles on the shell side.

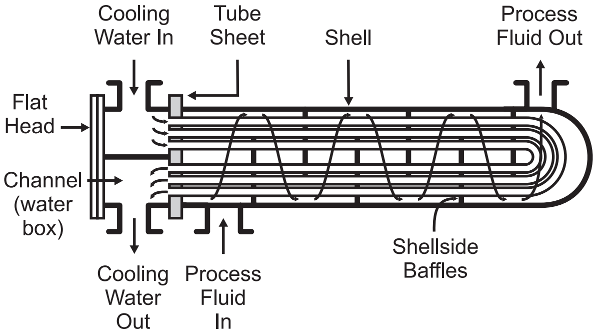


FIGURE 14.4 Assembly of a simple two-pass heat exchanger with water on the tube side and a U-tube bundle.

Heat exchangers fulfill a variety of generic heat transfer functions. Some functions include a change of state of either the process fluid or the coolant (or both), while others do not. These are a few of the important considerations made when determining the value contributed to a process by the cooling water:

- Exchangers condensing process liquids are the highest value exchangers in a chemical plant or refinery. Problems with condensing exchangers result in loss of production or environmental violations. If a leak violates environmental laws, immediate shutdown will incur excessive costs. Overhead condensers may provide a subcooled liquid for a separation tower reflux, which then requires additional heating. A hot reflux may result in off-specification product or causes reduced production in a separation tower.
- Surface condensers allow turbines to develop maximum vacuum. Loss of vacuum on the condensing side due to water-side fouling or scaling of the condenser will limit production or increase utility costs.
- Refrigeration condensers are found in all businesses. In the institutional market, the cost and maximum refrigeration capability are affected by condenser performance. In industrial plants, poor performance will have similar effects but are typically not recognized because the refrigeration systems are low priority. Ethylene plants use propylene as the working fluid, and refrigeration may limit production in the warmer months. The topic of refrigeration and chillers is covered in Chap. 39.
- Run-down coolers cool a stream leaving a unit going to storage. Normally, run-down coolers are low-value exchangers. The exception is when a stream is not sufficiently cooled and vent losses occur from the storage vessel.

No matter what type of exchanger is used, six factors will affect heat transfer in an exchanger:

1. Heat transfer characteristics of the metal—its thermal conductivity
2. Thickness of the metal
3. Heat transfer surface area
4. Velocity and turbulence of both the process stream and cooling water
5. Temperature difference between the process stream and the cooling water
6. Deposits of any kind on either side of the heat transfer surface

The first four of these are inherent in the design of the exchanger, while the last two are operational characteristics that change depending on the conditions of service. Deposits on either side of the barrier have lower thermal conductivity and reduce the efficiency of the heat exchanger (Fig. 14.5). This reduction of heat transfer efficiency means that the cooling water may not remove sufficient heat from the process. Therefore, production must be slowed or the flow of cooling water must be increased to maintain the same cooling rate available before fouling developed. Frequently, the latter is not possible, and the productivity of the process unit or the entire plant is reduced.

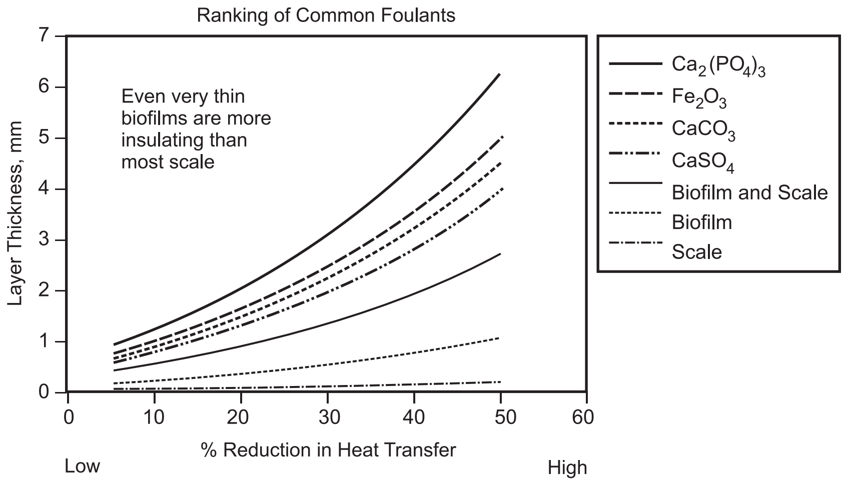


FIGURE 14.5 Insulating power of common foulants in heat exchangers.

Shell-and-Tube Heat Exchanger

Shell-and-tube heat exchangers come in a variety of shapes, sizes, and designs. Exchangers are typically classified by physical characteristics, such as the side in which the water flows (on the shell side or tube side), the number of passes on the tube side, the type of head (fixed or floating), or the type of bundle (U-tube or straight through).

Cooling water can be on either the tube side (inside the tubes) or shell side (surrounding the tubes) of an exchanger. From a water treatment perspective, there are significant advantages to having tube-side water. With this type of exchanger, water velocity is usually maintained above 2 to 3 ft/s (0.6–0.9 m/s) to as high as 7 to 8 ft/s (2.1–2.4 m/s), to help keep the tube walls free of suspended solids deposition. Lower water velocity encourages deposition of suspended solids in the tubes (Fig. 14.6). In a bundle of tubes, perhaps only one tube may have a low velocity due to plugging or poor distribution. Occasionally, high pressure on the process side can be handled more economically with cooling water on the shell side of the exchanger. One major problem in such exchangers is the low flow velocity frequently encountered around baffles, tube supports, and tube sheets, even when the average flow velocity through the shell appears acceptable. These low velocity areas influence skin

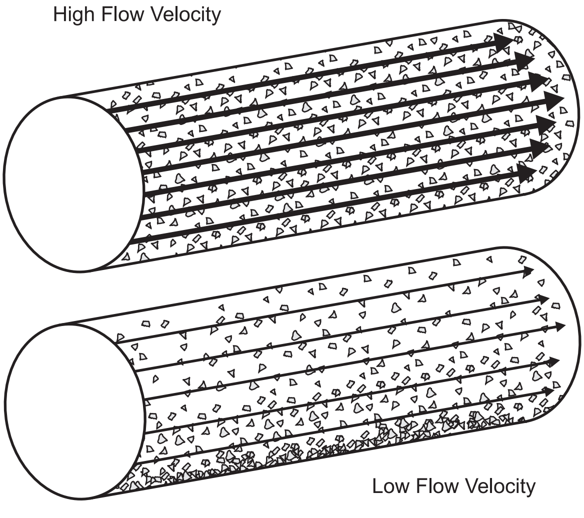


FIGURE 14.6 High flow velocity can help to keep insoluble particles suspended in the water, but low flow velocity will allow particles to settle onto the bottom of the tube surface.

temperature and greatly increase the potential for deposits and rapid metal deterioration. For example, critical mild steel exchangers with water on the shell side have been known to fail from perforations in as little as three months due to excessive deposition, even in the presence of a strong corrosion inhibitor.

Surface Condensers

Surface condensers are a special type of shell-and-tube exchanger found in electric utility operations and often in industrial plants, where a process fluid must be condensed. In the utility application, the primary function of a surface condenser is to reduce the turbine exhaust steam pressure and temperature to the lowest possible levels, thereby providing greatest turbine efficiency. A second function of surface condensers is to recover condensate and a small part of the exhaust steam heat. See Chap. 33 on the Power Industry for more details on surface condensers in utility applications.

Plate-and-Frame Heat Exchanger

These exchangers are constructed of a series of plates held in a frame and separated by gaskets and corrugations in the plates (Fig. 14.7). The total number of plates and the manufacturers stated area per

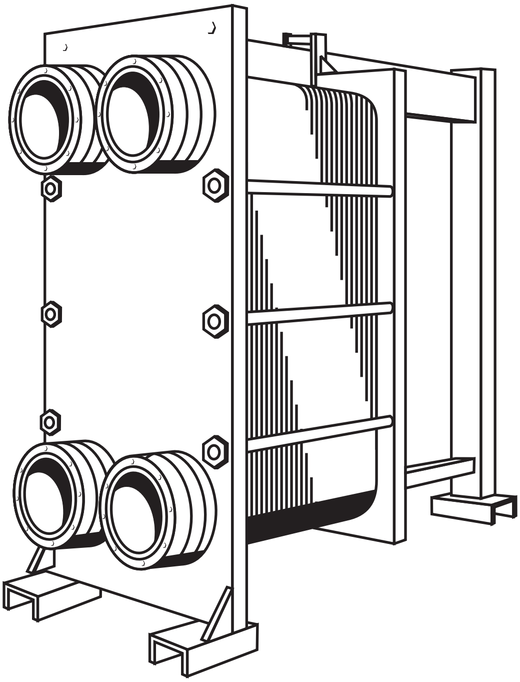


Figure 14.7 An assembled plate-and-frame heat exchanger.

plate determines the area of the exchanger. Plate-and-frame exchangers are a space-saving design, because these exchangers are typically much more compact than a shell-and-tube exchanger of the same surface area. Stainless steel and other corrosion resistant alloys can be used more economically because of the smaller size. However, fouling problems can be more severe because of the small flow passages for water between the plates. This can result in under-deposit corrosion or microbiologically influenced corrosion (MIC).

Spiral Flow Heat Exchanger

These exchangers are formed from either tubes rolled in a spiral or plates formed in a spiral. The exchanger formed by tubes is placed inside a shell through which the other fluid passes. The spiral plates allow the process to flow on one side of the plate and the cooling water to flow on the other side of the plate. End plates with gaskets prevent mixing of one fluid into the other. These types of exchangers are not common but have applications in condensate cooling and recovery and in cooling viscous fluids and slurries.

Reactor Jacket Cooling

Reactors, mix tanks, blend tanks, and other reaction vessels are often surrounded by jackets or coils that can heat or cool the vessel contents during processing. The jacket around the vessel, sometimes called an annular space heat exchanger, is typically an open space surrounding the vessel through which steam, cooling water, brine, or a combination of these fluids can flow. A number of jacket designs can be found in common use. Jackets can be plates welded around the outside of the vessel to form one compartment or multiple compartments segregated by baffles. Jackets can also be formed by welding half-pipe sections onto the outside of the vessel in a spiral pattern. Some reactor jackets have a dimpled appearance and are called a dimpled plate jacket.

Design and common usage of reactor jacket systems creates significant challenges for proper treatment and control of corrosion and deposition. The reaction vessel is often coated or constructed of a special alloy to resist corrosion. The jacket, however, is usually constructed of mild steel. This creates the potential for galvanic corrosion, where the steel jacket contacts the alloy of the reactor vessel walls. Low flow rates, irregular flow patterns, and restricted areas are common in the jacket space. Areas of low water flow may result in boiling or alternately wet and dry conditions that can result in severe water-side problems. In many cases, steam is used for heating to initiate reactions, and then cooling water is required to remove heat as the reaction progresses. Treatment of annular space heat exchangers is difficult under the best conditions, but treatment can be further complicated by the alternating use of steam and cooling water to heat and cool a reaction vessel.

Continuous Caster Mold

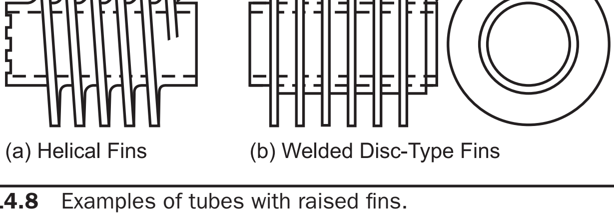
Continuous casting is the process in which molten steel is continuously poured into a mold that gradually solidifies the steel so that the formed steel shape is extruded out the bottom of the mold onto a work platform. The continuous caster mold is a unique heat exchanger, because of the exceptionally high amount of heat being transferred across a relatively small mold surface. Heat flux is often more than 1 million Btu/[h·ft^2] (3150 kW/m^2) and results in water-side skin temperatures of 250 to 300°F (120–150°C). This extremely high skin temperature is a strong driving force for scale formation. Scale deposits only a few mils (25.4 μm/mil) thick on the water side of the mold can result in serious problems, such as a poor quality cast, or worst of all, breakout of molten steel through the mold wall.

Special Tube Applications

Some heat exchangers contain special tubes to improve heat transfer efficiency. These are generally used in special applications, and the tube enhancement may be on the process side or the water side of the exchanger. Excessive deposition and under-deposit corrosion may occur on the tube surface, depending on the type of tube and whether the cooling water contacts the fins or grooves on the tubes. Examples of some of these tube enhancements are shown as follows.

Raised Fin Tube Heat Exchangers This modification provides increased external surface area by means of fins on the outside of the tube. The fins may appear as discs, helical fins like screw threads, or longitudinal fins (Fig. 14.8). The fins may be either welded or peened to the surface of the tube. Air handlers, radiators, and fin-fan coolers are examples of exchangers using raised fins.

Integral Low Fin A tube commonly found in refrigerant condensers and hydrocarbon process plants is called an integral low-fin tube (Fig. 14.9). A standard tube is formed with small fins on the outside of the tube such that the outside diameter conforms to a standard tube dimension. The ends of the tube are left bare where the tube passes through the tube sheet.



(a) Helical Fins (b) Welded Disc-Type Fins

Figure 14.8 Examples of tubes with raised fins.

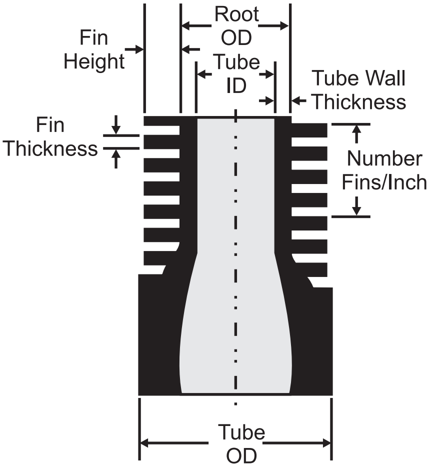


Figure 14.9 Example of an integral low-fin tube.

Rifled Tubes Rifled tubes are used in some refrigeration equipment where either chilled water or condenser water flows through the tube. "Rifling" refers to cutting spiral grooves along the length of the inside of the tube. Theoretically, rifling increases turbulence and subsequently the heat transfer coefficient. The equipment manufacturer can provide a smaller evaporator or condenser due to the increase in the heat transfer coefficient. The grooves in the tube must be kept very clean to achieve the desired effect on heat transfer. Fouling of the grooves will decrease heat transfer and lead to severe under-deposit corrosion. Cleaning of the tubes is difficult, and the grooves must remain sharp and clean to produce the increase in heat transfer. Figure 14.10 shows an example of a rifled tube with deposition covering localized corrosion sites in the grooves.

Calculations and Measurements

Performance monitoring of heat exchangers is essential to understand the operation of a system and obtain best results from any treatment program. Several design parameters should be calculated and compared to the original system design to determine if changes have occurred. Many of the measurements and calculated performance values should be determined over a period of time and evaluated with trend analysis tools. Examples of some of the more common parameters and how these calculations can be used will be described.

Approach Temperature

This value is easy to determine if water and process temperatures are measured for an exchanger. Approach temperature can be used as a first step in monitoring performance of exchangers where

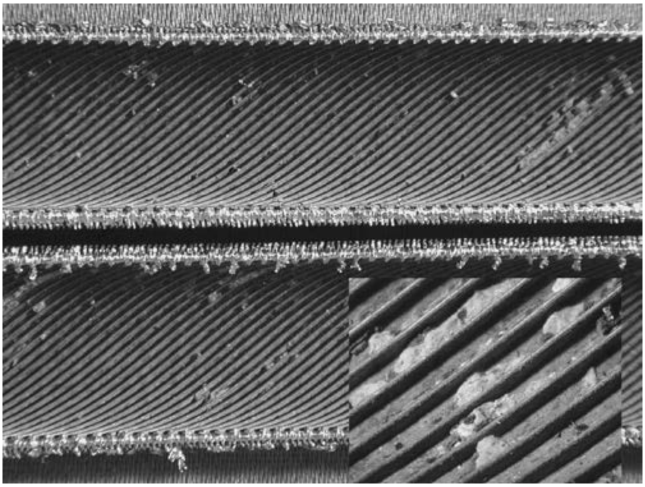
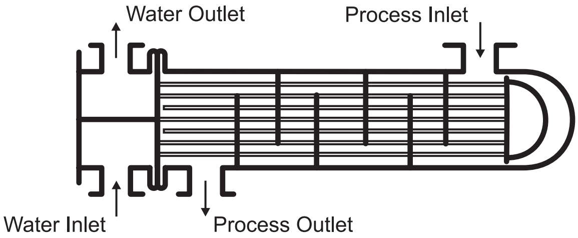


Figure 14.10 Rifled condenser tube removed from a refrigeration chiller and split longitudinally. The deposits are the result of localized corrosion in the grooves. The inset image shows an enlargement of part of the tube to illustrate how the deposit over the corrosion sites can fill the grooves.

condensation does not occur or in process condensers where the condensate is not cooled below the condensation temperature (no subcooling of the condensate). The simplest definition of approach temperature is the difference between the process outlet temperature and the cooling water inlet temperature (Fig. 14.11). The closer these two temperatures approach each other, the greater the cooling efficiency of the exchanger. Approach temperature is sensitive to changes in both water and process flow, and temperature, and is only a rough indicator of exchanger performance.



Approach Temperature =
Process Outlet Temperature – Water Inlet Temperature

Figure 14.11 Approach temperature can be calculated easily if water inlet and process outlet temperatures are available.

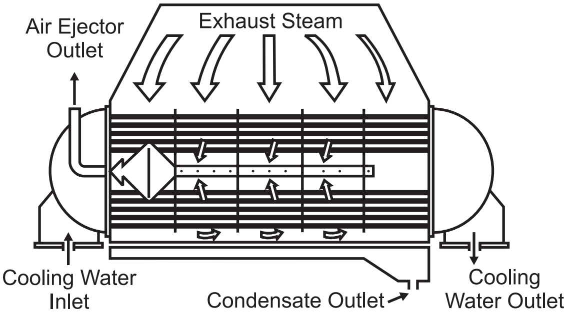


Figure 14.12 Terminal temperature difference (TTD) is the difference between the exhaust steam saturation temperature and the cooling water outlet temperature.

Terminal Temperature Difference (TTD)

This calculation is valuable in condensers, where further cooling below the condensation temperature is not desired. TTD is the difference between the gas condensing temperature and the cooling water outlet temperature, as shown in Fig. 14.12. The most common example of this is in steam condensers in electric utility plants, where minimal subcooling is desired, so that less heat is needed to create steam again from the condensate. In a steam condenser, TTD is the difference between the saturation temperature of the exhaust steam and the cooling water outlet temperature.

Reynolds Number

Water flow through a heat exchanger tube is not uniform. More water, at a higher velocity, moves through the center of a tube than at the tube wall. The water at the tube surface is flowing very slowly and is referred to as the static film of water (Fig. 14.13).

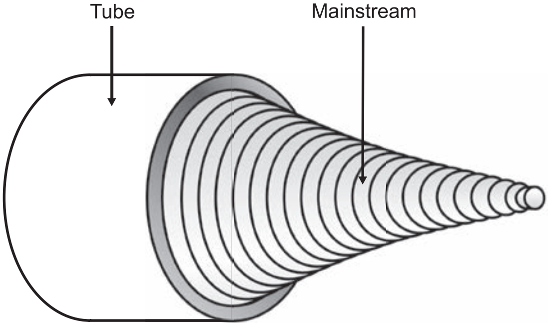


Figure 14.13 The water velocity profile in a tube will have the highest velocity at the tube center.

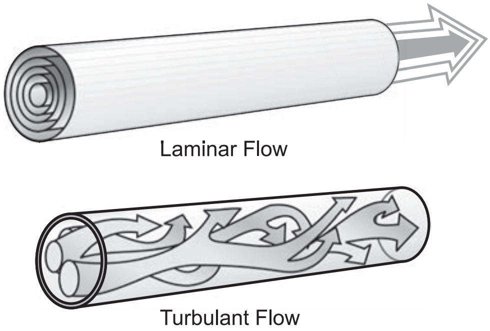


FIGURE 14.14 Laminar versus turbulent flow.

In addition to the velocity and mass flow differences between the center and surface of a heat exchanger tube, there is another important variable that must be considered: the nature of the flow. Fluid flow can either be laminar or turbulent (Fig. 14.14). Turbulent flow decreases the thickness of the static film next to the tube wall, promotes mixing, and increases the rate at which heat is absorbed by the cooling fluid.

The Reynolds number is a dimensionless number that provides an indication of whether flow is laminar or turbulent. The Reynolds number can be calculated using Eq. (14.1) (U.S. units) or Eq. (14.2) (metric units):

$$R_e = d\nu/12\nu' \tag{14.1}$$

$$R_e = 100d\nu/\nu' \tag{14.2}$$

where R_e = Reynolds number (dimensionless)
d = tube inside diameter (ID), in. (cm)
ν = liquid velocity, ft/s (m/s)
ν' = liquid kinematic viscosity, ft²/s (cm²/s)

An example calculation of the Reynolds number for a heat exchanger with tube ID of 0.787 inch (2 cm) and velocity of 3.3 ft/s (1 m/s) is shown. The liquid is water at 100°F (38°C) with kinematic viscosity of 7.33×10^{-6} ft²/s (6.811×10^{-3} cm²/s).

U.S. Units

$$R_e = (0.787 \text{ in.})(3.3 \text{ ft/s})/[(12)(7.33\times10^{-6} \text{ ft}^2/\text{s})] = 29\,500$$

Metric Units

$$R_e = (100)(2 \text{ cm})(1 \text{ m/s})/(6.811\times10^{-3} \text{ cm}^2/\text{s}) = 29\,400$$

As stated previously, the purpose in calculating the Reynolds number is to determine whether the flow through a tube is laminar or turbulent. The guidelines that follow apply to the majority of cases:

- If R_e is less than 2100, flow is laminar.
- If R_e is 2100 to 4000, flow may be laminar or turbulent.
- If R_e is greater than 4000, flow is turbulent.

Coefficient of Heat Transfer (*U*-value)

The coefficient of heat transfer, or *U*-value, is one of the best indicators of heat exchanger performance and efficiency. *U*-value is much less sensitive to changes in process flow, process temperature, and coolant temperature than many of the other indicators commonly used. Except for extreme changes in process flow or temperature, increases or decreases in *U* will usually reflect real differences in the cleanliness of the exchanger. However, changes in *U* can reflect changes in the cleanliness of the process side as well as the water side (Fig. 14.15).

The heat transfer coefficient or *U*-value is calculated using Eq. (14.3).

$$U = Q/[(A)(\text{LMTD})] \tag{14.3}$$

where U = heat transfer coefficient, Btu/[h · ft^2 · °F] (kW/[m^2 · °C])
Q = heat duty, Btu/h (kJ/h or kW)
A = heat transfer area of exchanger, ft^2 (m^2)
LMTD = log mean temperature difference, °F (°C)

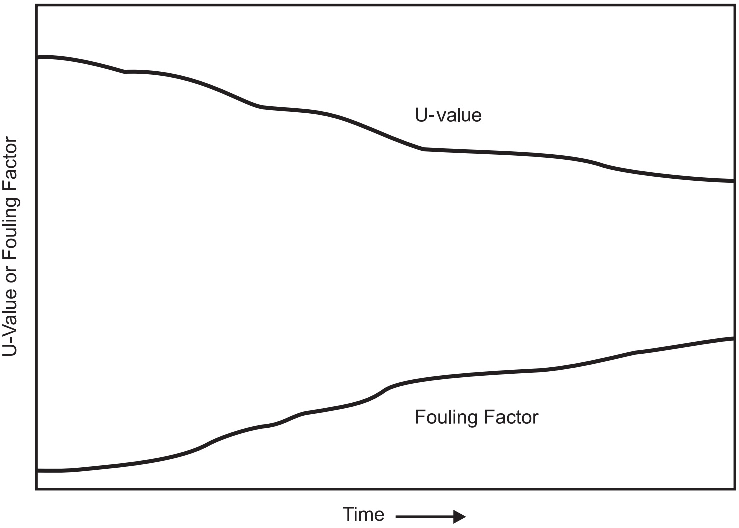


Figure 14.15 Decreasing *U*-value can indicate fouling in an exchanger. A fouling factor trend curve for a heat exchanger is the inverse (reciprocal) of the *U*-value curve.

Note that a correction factor is usually applied to LMTD for multipass exchangers, based on the configuration of the exchanger.

Normally, heat exchangers will have *U*-values in specific ranges depending on the type of fluids on both sides of the exchanger and whether condensation is involved. Here are typical *U*-value ranges for different heat exchange processes:

- *U*-value range for gas-liquid heat exchange is 50 to 150 Btu/[h · ft^2 · °F] (0.3–0.9 kW/[m^2 · °C]).
- *U*-value range for liquid-liquid heat exchange is 100 to 300 Btu/[h · ft^2 · °F] (0.6–1.7 kW/[m^2 · °C]).
- *U*-value range for condensers is 400 to 600 Btu/[h · ft^2 · °F] (2.3–3.4 kW/[m^2 · °C]).

Fouling Factor

The fouling factor for any heat exchanger, is a measure of how the present coefficient of heat transfer compares with either the design coefficient of heat transfer, or the coefficient of heat transfer immediately after the exchanger was cleaned down to the bare metal on both the water and the process sides. Fouling factor is calculated using Eq. (14.4).

$$f = 1/U_c - 1/U_d \tag{14.4}$$

where f = fouling factor, [°F · ft^2 · h]/Btu ([°C · m^2]/kW)
U_d = *U*-dirty, Btu/[h · ft^2 · °F] (kW/[m^2 · °C])
U_c = U-clean, Btu/[h · ft^2 · °F] (kW/[m^2 · °C])

Typically, fouling factors are in the range of 0.001 to 0.005 [°F · ft^2 · h]/Btu (0.18–0.88 [°C · m^2]/kW).

If a design *U* or a design fouling factor is not available for a given exchanger, fouling factor can still be calculated. The design *U* may be calculated by using the process flow, process temperature, and water temperature originally specified for the exchanger. Subtracting the reciprocal of this *U*-design from the reciprocal of the present *U*-value for the exchanger will yield the present fouling factor with a reasonably high level of accuracy in most cases. Corrected LMTD should be used in the calculations.

C Factor

C factor is a calculation to relate flow through an exchanger to the pressure drop (ΔP) available across the exchanger. Flow through a clean exchanger is related to the ΔP by Eq. (14.5).

$$F = (C_\mathrm{clean})(\Delta P^{0.5}) \tag{14.5}$$

where F = flow, gpm (m^3/h)
C_{clean} = constant calculated from design flow and clean ΔP
ΔP = Pressure drop across the exchanger due to the flow, psig (kPag)

Rearranging the formula, C factor is variable and is calculated from the actual flow and ΔP. This variable C factor (called C_{foul}) now indicates the loss of heat transfer as fouling occurs and is calculated using Eq. (14.6).

$$C_{\text{foul}} = F/(\Delta P^{0.5}) \tag{14.6}$$

Some points to remember about the C factor are:

- C factor is not dimensionless and will be dependent on the design flow and calculated clean pressure drop at design flow.
- C factor is a function of the cleanliness of the exchanger tubes. The C factor will decline with time, if fouling or scaling result in narrowing of the inside diameter of the tube.
- C factor is suitable for monitoring tube-side cooling water exchangers with tube outside diameter (OD) of less than 1.0 inch (25.4 mm).
- In some cases, shell-side cooling water geometry will also show a decrease in C factor, if uniform scaling or fouling causes narrowing of the spaces between the tubes.
- Neither tube-side nor shell-side cooling water will show a significant decrease in C factor, if only silting of the exchanger occurs and ΔP does not change.

The design clean ΔP is calculated using the design flow and clean heat exchanger geometry. The actual differential pressure (ΔP) is determined by the total hydraulics, including the circulating water pumps and throttle valves in the system. If gauges are used to measure actual ΔP, each gauge reading must be corrected for the difference in elevation above a common point. Figure 14.16 illustrates how the correction to pressure reading is done, if the gauges are at different elevations. Only one of the two pressure readings must be corrected.

Skin Temperature and Water Velocity

As mentioned in the beginning of this chapter, skin temperature and water velocity in the exchanger are critical parameters for determining the stress in any cooling system. Skin temperature and water velocity are difficult to calculate and beyond the scope of this book. These parameters depend on characteristics of the exchanger,

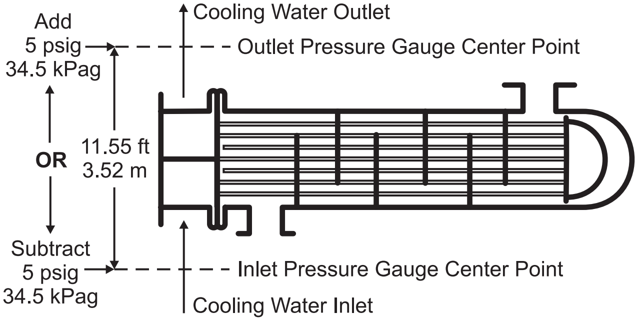


Figure 14.16 For every 2.31 ft (0.70 m), 1 psig (6.9 kPag) must be added to the value from the upper pressure gauge or subtracted from the value from the lower pressure gauge.

such as whether water is on the tube or shell side and whether the water and process flow co-currently or counter-currently through the exchanger. These values are often specified as part of the design characteristics of a heat exchanger. These parameters should be determined under current operating conditions to compare to the design specifications.

Cooling water temperature varies throughout the cross section of a tube; the hottest water is nearest the tube wall. The temperature of the tube wall, called the skin temperature, is important in selecting chemical treatment programs. In fact, skin temperature is the most important variable controlling corrosion and deposition on the tube surface. The skin temperature is defined by water velocity, heat flux, water temperature, process temperature, and thermal conductivity of the tube wall. Areas of high skin temperatures [above 200°F (93°C)] are the most probable locations for scale formation and corrosion. Many compounds found in water-formed deposits are less soluble at increased temperature, and corrosion reactions proceed faster as temperature increases.

Effects of Corrosion and Deposits

Problems created by the interaction of the water and cooling system components can reduce the efficiency of the heat transfer process. These problems include corrosion of system metals and deposition on surfaces in heat exchangers, system piping, or the cooling tower. Deposition can be due to corrosion products, scale-forming minerals, suspended solids, and bacteria in the water. Both thermal and hydraulic performance of a cooling system is decreased by deposition. More details on these problems can be found in Chap. 15 on

Cooling Water Deposition, Chap. 16 on Cooling System Corrosion, and Chap. 17 on Cooling Water Biology.

Corrosion and deposition affect the efficiency of the cooling system. If corrosion and deposition are not kept under control, heat exchangers will soon become inefficient, and equipment will be ruined. Efficiency loss and equipment failure cost money in terms of increased maintenance, equipment repair, or replacement, or lost production. In extreme cases, safety problems that cost jobs or lives may result. Examples of these problems include the following:

- Reduced heat transfer efficiency—Clean heat exchangers, free of corrosion and deposits, allow a plant to operate at peak production. Corrosion and deposition on heat transfer surfaces reduce the ability to remove heat from the process. Production goes down while operating costs go up.
- Increased maintenance and cleaning—Corrosion products and other deposits cause fouling in heat exchangers and transport piping. The standard way to remove deposits is to take the system off-line for cleaning. System cleaning requires time and personnel to do the job right. Time is money when a unit is out of production.
- Equipment repair and replacement—If corrosion is severe, system piping or heat exchanger tubes may develop leaks. Again, the system operation must be stopped for repair. Some heat exchanger tubes may be taken out of service by plugging the tube. With others, the only choice is to re-tube or replace the entire exchanger, which is a costly operation.
- Process-side or water-side contamination—When leaks occur because of corrosion, serious problems result on both sides of the heat exchanger. Cooling water may leak directly into the process stream, contaminating product, leading to loss of production and wasted product. Disposal or rework of contaminated product can be very expensive. The process stream leaking into the cooling water may create even more deposits, fouling, and corrosion.
- Unscheduled shutdown—Corrosion and deposition in the cooling system can unexpectedly stop operation of an entire plant. The cost of water, maintenance, and system repair seems small, when compared to the dollars lost due to the loss of production.

The net impact of poorly controlled corrosion and deposition is increased operating costs and reduced profitability for any facility with a cooling system. However, there are some examples of fouling that are normal or not always caused by interaction of the water and the system components.

Normal Surface Film Formation

A normal loss in heat transfer will occur when a new or recently cleaned exchanger is put in service. A surface film will form on a clean tube, even under normal, well-inhibited conditions. The tube narrows in diameter as the deposit forms, and the velocity of the cooling water increases. This surface film of deposit will decrease the cooling water skin temperature because of the insulating effect of the film. The increased flow also tends to decrease the skin temperature and retards further formation of deposits. If the exchanger is sized properly, the exchanger performance will normally plateau at a capability that will economically satisfy the process requirements. In most cases, heat exchangers are oversized by design to account for this normal deposition. This leveling of performance indicates an acceptable treatment program is in place. More than 85% of the exchangers in a unit should operate three to four years before cleaning. However, if further deposition occurs, the performance of the exchanger will suffer as *U*-value decreases with greater deposit thickness.

Mechanical Causes for Plugged Tubes

Trash, pieces of broken fill, pieces of scale, or corrosion products will deposit on the tube sheet, plugging tubes and thereby reducing heat transfer area and cooling water flow. Proper backwashing techniques will recover the lost performance but must be done on a scheduled basis. Backwashing should be timed to occur before significant performance loss is noted. Additional equipment including Y-strainers, basket strainers, and special strainers installed in the inlet of the exchanger may be required in severe cases.

Types of Cooling Water Systems

Heat transferred to the water from the process in a heat exchanger must then be rejected to the environment. This is the role of the cooling water system. There are three basic types of cooling water systems: once-through, closed recirculating (nonevaporative), and open recirculating (evaporative) systems. The type of cooling system defines how the heat is rejected to the environment.

In nonevaporative systems like once-through and closed cooling water systems, heat rejection is governed by the specific heat capacity of water (1 Btu/[lb · °F] or 4.19 kJ/[kg · °C]). In a cooling tower system, where water is evaporated, the phase change from liquid to gas dissipates about 1000 Btu/lb (2300 kJ/kg) of water converted to vapor. Evaporative systems can dissipate 50 to 100 times more heat to the environment per unit of water than a nonevaporative system.

A short description of each cooling water system is given as follows. Open recirculating cooling tower systems are covered in more detail, because these systems are the most dynamically complex.

Once-through Cooling Water Systems

Once-through water is taken from the water source, passed through the cooling system, and returned to the receiving body of water. Heat picked up from the process is rejected by nonevaporative cooling. Heat picked up in the once-through water is often beneficial for process use, such as in Paper Mills, reducing the need for heating the water by other means. The chief characteristic of once-through cooling water systems is the relatively large quantity of water used. A simple flow diagram for a once-through cooling water system is shown in Fig. 14.17. Some once-through systems use plant water for drinking as well as cooling, thereby requiring chemical treatment that is safe for potable use.

There are many examples of once-through systems, although not all of these applications are cooling systems. The use of once-through cooling water has decreased due to the environmental effects of the discharge and inability to treat the systems economically for corrosion and deposition. In some parts of the world, once-through systems may be used in electric utilities, paper mills, refineries, chemical plants, and steel mills.

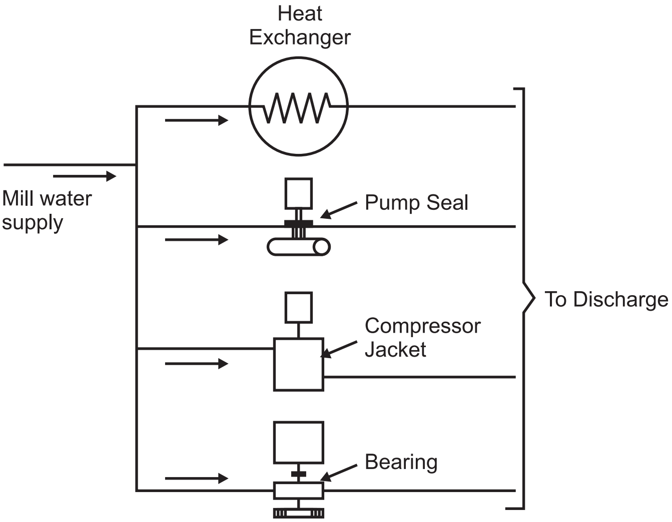


Figure 14.17 Typical service for a once-through cooling system.

Examples of Once-through Systems

Many industries use water as an essential component of the manufacturing process in addition to cooling purposes. In some cases, the volume of water usage is a large part of the process. Many food industry processes use water for washing at some stage of product processing. Examples of once-through cooling and process water applications are:

- Electric utilities—Condenser cooling is the largest water use in the power generation process. A utility may be situated on a river or use a large impounded lake as a once-through cooling water source. Process heat can be dissipated without having the expense of building and operating a cooling tower. An impounded lake is technically a recirculating cooling system; however, because of the large quantities of water involved, the system must be treated like a once-through system.
- Paper mill systems—Paper mills require large volumes of water for cooling plant equipment and the papermaking process. For example, the fiber slurry leaving the headbox on the paper machine is 99% water and only 1% fiber. Water availability and quality are essential components of paper manufacture. The same water system may supply both the cooling and process water.
- Steel mills—Large volumes of water are required in primary metals manufacture because of the cooling requirements of the molten metals. While some of these systems still use once-through water, many have been converted to recirculating systems with cooling towers. This conversion was necessary for environmental reasons.
- Food plants—Very stringent water quality specifications apply in the food industry, where rigorous regulations have been established to minimize possible adverse health effects. In this case, the impact of water quality on the process may be significant. In most cases, the potable water used for the process is kept separate from cooling water systems.
- Municipal or potable water systems—Facilities that produce drinking water for industry and residential communities must meet all potable standards for the particular country. While these are once-through systems, cooling applications are generally not involved. The main problems in these systems are corrosion and scaling of the system piping and iron and manganese contamination that reduces the water quality for the user.

Other types of systems may be occasional once-through systems. For example, most industrial facilities have firewater systems that are separate from normal operating processes. This water source may occasionally be used for makeup water to a cooling system or for wash water. However, the water is mostly held in a static condition within the system. Static or non-flowing systems present unique treatment challenges and are not covered in this chapter.

Cooling Lakes or Ponds

Man-made lakes are sometimes used for electric utility condenser cooling, particularly in the United States. These lakes are often created by building a dike around a large area of land. This area is then filled with water from a river. The lake may also be called impounded or perched lakes. The total water volume of the lake system is such that the condenser cooling water must be treated like a once-through system. However, these lakes recycle the water used for cooling. Makeup is often drawn from a river and there may be no blowdown, other than seepage through the lake bottom. Some cooling of the lake occurs by heat loss to the environment and some by direct evaporation from the surface of the water. Dissolved salts in man-made lake water can slowly concentrate above the concentration of the makeup water. The concentration effect may be higher in summer than in winter, if evaporation rates are different.

The pH and alkalinity of the lake can be affected by a number of factors. As the lake water concentrates, the typical dissociation of bicarbonate (HCO_3^-) into carbonate (CO_3^{-2}) and carbon dioxide (CO_2) can occur. (See Chap. 4 on Water Chemistry for an understanding of alkalinity relationships.) Some of the CO_2 will be lost to the atmosphere by equilibration, driving up the lake water pH. During daylight hours, algae can consume some of this CO_2 by photosynthesis, further pushing the bicarbonate/carbonate equilibrium to produce higher carbonate levels and higher pH. Respiration of bacteria and other oxygen consumers will release CO_2, but generally not enough to counterbalance the effect of algae. The net impact may create diurnal cycles, where pH increases during daylight hours and decreases at night. Alkalinity and pH levels can increase to the point where calcium carbonate scale formation is a problem.

Problems in Once-through Systems

Water-related problems can be unique in once-through systems, because of the large volume of water used and specific characteristics of the water source. There are two main sources of water—groundwater and surface water.

Water pumped from below the surface of the earth using a well is groundwater. Groundwater characteristics vary depending on the type of rock below the surface that surrounds the water. Groundwater generally has higher levels of dissolved minerals than surface water at the same locale (Table 14.1). The reason is that groundwater has a very long contact time with the minerals in the ground. In some

Constituent (mg/L Except Conductivity)	Well Water Ames, IA, U.S.	Green Valley Lake Creston, IA, U.S.
Calcium ($CaCO_3$)	360	89
Magnesium ($CaCO_3$)	170	60
Total hardness ($CaCO_3$)	530	149
Iron (Fe)	2.2	1.7
Manganese (Mn)	0.41	0.1
Silica (SiO_2)	27	7.2
Sodium (Na)	41	11
Chloride (Cl)	92	12
Sulfate (SO_4)	160	11
M alkalinity ($CaCO_3$)	330	120
P alkalinity ($CaCO_3$)	<1	<10
Conductivity (μS/cm)	1200	300

Table 14.1 Groundwater and Surface Water in a Similar Geological Region

areas, the higher dissolved solids can be corrosive ions like sulfate and chloride. In other areas, the mineral content may be calcium, magnesium, and high alkalinity that can form scale in a cooling system. High silica concentrations exist in well water in localized parts of the world. Silica can cause either amorphous silica scale or magnesium silicate scale, depending on the other characteristics of the water and the system. Some wells have high amounts of dissolved gases like CO_2 or hydrogen sulfide (H_2S) that can be corrosive. Metal ions like iron and manganese are often present as soluble ions in groundwater sources. These metal ions may be oxidized to insoluble forms after the water is brought in contact with air and precipitate in cooling systems.

Surface water quality is not as uniform as groundwater. In fact, the variability of surface water is the major challenge for industrial water treatment applications. Suspended solids or turbidity in a surface water supply is highly variable, with rapid changes possible depending on upstream or climatic events. Variations in turbidity require a flexible treatment program to handle the variable foulant loading. Temperature variability occurs seasonally, but also in much shorter periods, depending on conditions upstream from point of use. Subcooling of the process fluid may occur if water temperature is too cold, resulting in throttling (reducing) cooling water flow through an exchanger. Throttling the water flow can cause an increase in fouling due to the low water velocity. Cooling capacity may be impossible to recover, when the source water becomes warmer again and water flow through the exchanger is increased.

Seawater and brackish water are unique water sources that can contain high dissolved solids, mostly consisting of sodium and chloride ions. Because the high dissolved solids can be very corrosive, heat exchangers or condensers are normally made of corrosion resistant alloys like aluminum brass or metals like titanium. Distribution lines are normally coated mild steel or nonmetallic materials. Seawater is generally very consistent around the world. The total dissolved solids (TDS) range of seawater is 34 to 36 g/L in most oceans. Brackish water may come from surface or groundwater sources. Brackish water can contain 0.2 to 50 g/L total dissolved solids or more. Some well waters can be considered brackish, due to high concentrations of sodium carbonate or sodium chloride present in the water (Table 14.2).

Unique biological problems can result from the use of groundwater or surface water in once-through systems. Well water can contain anaerobic bacteria that can cause localized corrosion. Surface water, particularly seawater, presents problems from growth of macro-organisms like clams or mussels in a cooling system. The control of large species (macro-organisms) in once-through water systems is very challenging. The organisms can grow rapidly once attached to a

Constituent (mg/L Except Conductivity)	Deep Well Bridgeport, TX, U.S.
Barium (Ba)	14
Boron (B)	10
Calcium ($CaCO_3$)	5500
Magnesium ($CaCO_3$)	1300
Total hardness ($CaCO_3$)	6800
Iron (Fe)	4.4
Manganese (Mn)	1.3
Potassium (K)	220
Silica (SiO_2)	<26.1
Sodium (Na)	12 000
Strontium (Sr)	380
Chloride (Cl)	25 000
Sulfate (SO_4)	57
M alkalinity ($CaCO_3$)	2700
P alkalinity ($CaCO_3$)	1100
Conductivity (µS/cm)	62 000

Table 14.2 Example of Brackish Well Water Composed Primarily of Sodium Chloride

cooling system. Macrofouling can cause damage to pumps, restrict water flow, and plug heat exchanger tubing, resulting in lost cooling capacity. See Chap. 17 on Cooling Water Biology for more information on macrofouling.

Closed Recirculating Systems

Closed recirculating systems are generally very simple. However, these systems can become the most difficult to maintain once problems occur. A closed recirculating system is one in which the water is circulated in a closed loop with negligible evaporation, exposure to the atmosphere, or other influences that would affect the chemical or biological properties of the system water. In closed recirculating systems, heat is transferred to the cooling water from the hot process, and then the heat is transferred from the cooling water to the environment in another piece of heat transfer equipment (Fig. 14.18). In closed cooling systems, the heat is usually dissipated by an open recirculating cooling system or by air-cooling in a fin-fan cooler.

Closed System Characteristics

There are many different types of closed systems used in a wide variety of applications, from building heating and cooling to primary metals applications. Example criteria that define when a closed system is used instead of an open system include:

- A critical process, where cooling water system failure creates serious problems.
- An extremely hot process, where scale formation on heat transfer surfaces must be eliminated.
- A coolant temperature below ambient or below 32°F (0°C) is necessary.
- A water temperature above boiling is required (e.g., pressurized hot water systems).
- A higher degree of control is required.

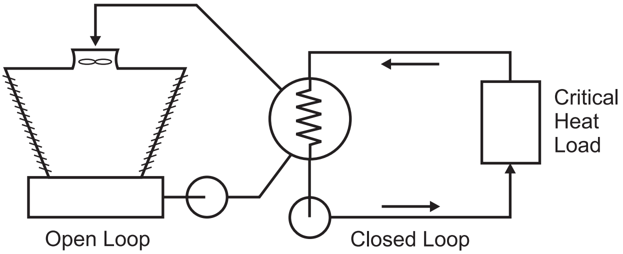


FIGURE 14.18 A closed cooling system is often used for critical heat transfer applications. In this case, the closed system water is cooled by an open cooling tower system.

Closed cooling systems can be used in refrigeration systems with temperature below freezing, or for cooling high heat flux systems like a continuous steel casting mold. Closed cooling systems may have unique characteristics such as:

- The systems contain a variety of metals, often connected together forming galvanic couples. (See Chap. 16 on Cooling System Corrosion.) Metals include mild steel and copper alloys, with occasional use of aluminum, stainless steel, etc.
- Systems are designed for minimal makeup and blowdown but do not often achieve minimal water losses.
- Since these systems are not designed for blowdown, filtration of the recirculating water is recommended.
- System volumes range from as small as 10 gal (0.04 m^3) to more than seven million gallons (26 500 m^3).
- Some systems are operated with intermittent idle periods, where no water flow exists.

Problems in Closed Recirculating Systems

Closed cooling water systems suffer the same problems as other cooling water systems, that is, corrosion, deposition, and microbial growth. The major performance-related problems in closed systems are most often due to water leakage or microbial problems. Corrosion can usually be controlled to very low rates of metal loss, because inhibitor treatments can be maintained at high dosages. Similarly, scale can be minimized by use of softened makeup water. However, water loss from leakage or microbial degradation of inhibitors can cause increased corrosion and scale.

Theoretically, under the conditions that exist in a truly closed recirculating system, all of the common scale-forming constituents in the system water (such as calcium carbonate, calcium sulfate, magnesium salts, and silica) can deposit on metal surfaces without any noticeable results because such small quantities are involved. However, in the more typical system, water leakage creates demand for more makeup water that brings additional scale-forming ions into the closed system water. Continued precipitation with each new increment of water added to the system can cause significant scale formation, plugged water passages, and reduced heat transfer.

It may seem that because the average closed system sees little sunlight, has low oxygen content, and contains few nutrients, there should be no problem with microbial growth. In reality, microbial growth can be severe for several reasons. Leakage causes higher makeup rates, which introduces more oxygen, debris, and nutrients and inoculates the system with new microbial organisms. Process leaks can provide high amounts of food for microorganisms.

Many closed systems have tanks that are open to the atmosphere, or have entrainment of air at seals, so oxygen levels can be at or close to saturation. Finally, some microbial organisms can use some corrosion inhibitors like nitrite as a food source. All of these factors illustrate how microbial problems can occur in closed cooling water systems. Microbial problems contribute to fouling, corrosion, and loss of heat transfer. In fact, biofilms are among the most insulating deposits encountered on heat transfer surfaces (refer to Fig. 14.5 shown earlier).

Another problem is that closed cooling systems are rarely equipped with continuous monitoring or automated control systems. This situation may lead to neglect of the system, because of the false impression that system conditions and product dosage should be constant. However, system conditions can change quickly due to leakage or microbial contamination. For this reason, continuous monitoring and control systems, are very valuable for best results and lowest total cost of operation.

Open Recirculating Systems

An open recirculating system incorporates a cooling tower, evaporative condenser, or evaporation pond to dissipate the heat removed from the process or product. An open recirculating system (Fig. 14.19) takes water from a cooling tower basin or pond, passes the water through process equipment requiring cooling, and then returns the water through the evaporation unit, which cools the water that remains. The open recirculating system repeats this process of reuse, taking in sufficient freshwater makeup to balance the water evaporated and water blown down from the system to control the chemical character of the recirculating water. This reuse of water greatly reduces water demand (e.g., withdrawal from a river) and discharge or blowdown. With the severe water availability issues that we face today, reducing the amount of water used as makeup to cooling towers is a major concern, and the focal point of many innovations in water treatment.

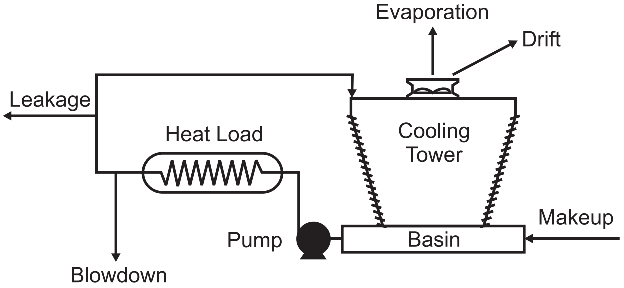


Figure 14.19 Typical open recirculating system using a cooling tower for heat rejection by evaporation of water to the atmosphere.

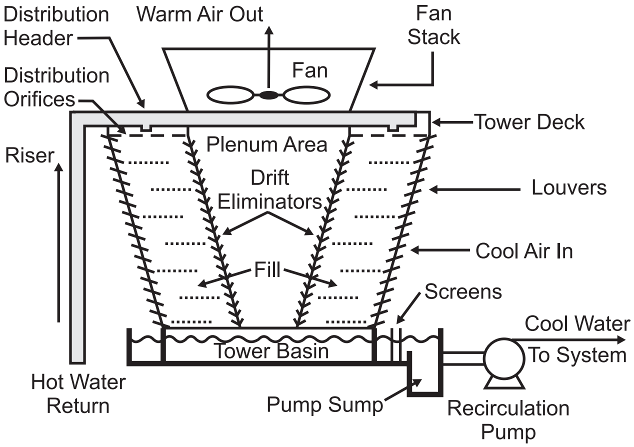


Figure 14.20 Example of the basic components of a cooling tower (crossflow) that create the contact between air and water to cause evaporation and cool the water.

Cooling Tower Systems

These common open recirculating systems are designed to evaporate water by intimate contact of water with air. Cooling towers are classified by the method used to induce airflow (natural or mechanical draft) and by the direction of air flow (counterflow or crossflow relative to the downward flow of water). The basic components of a crossflow cooling tower are shown in Fig. 14.20. These components are common to most cooling towers, but the configuration may be different in other cooling tower designs.

Airflow in natural draft towers is created by the difference between air density inside the tower and the surrounding atmosphere. The warmer, more humid air inside the tower has lower density, which establishes the airflow. Wind velocity also affects performance. Most natural draft towers in modern utility service are of hyperbolic design. These tall towers provide cooling without fan power and minimize plume problems and drift.

Mechanical draft cooling towers use fans to move air, instead of depending on natural draft or wind. This speeds the cooling process and increases the efficiency of the tower by increasing the air velocity over droplets of water falling through the tower. Mechanical towers can, therefore, evaporate much more water than natural draft towers of the same size. There are two designs of mechanical draft towers, forced and induced draft. Fans mounted on the side of forced draft towers, force air through the tower packing, mixing air with the falling water (Fig. 14.21).

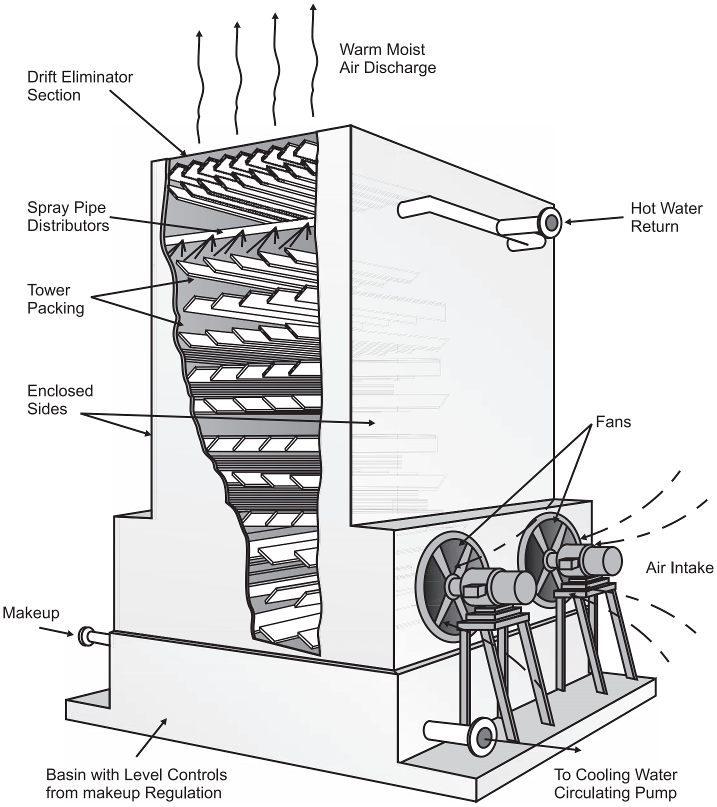


FIGURE 14.21 Forced draft cooling towers have the fans blowing air into the tower.

Induced draft cooling towers are either counterflow or crossflow with fans on top of the tower pulling cooling air up through or horizontally across the falling water. Figure 14.22 shows examples of counterflow and crossflow towers. The choice between forced draft and induced draft is based on engineering considerations that take prevailing weather patterns into account. A major consideration is to avoid recirculation of the warm air discharge, which would greatly reduce tower performance. The main advantage of a counterflow tower is that the coldest water contacts the driest air, providing the most efficient evaporation.

The operating characteristics of cooling tower systems create a very dynamic environment. The factors that contribute to this dynamic nature include:

- Evaporation, which concentrates the ions in the water left behind

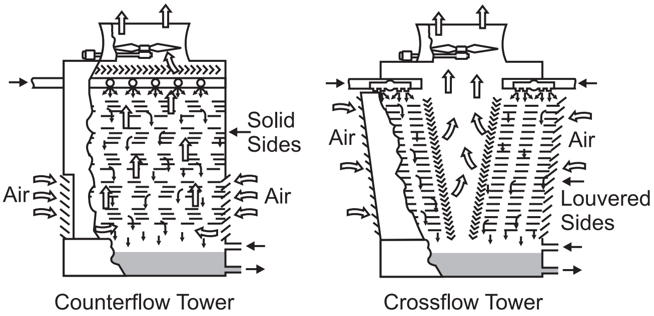


FIGURE 14.22 Examples of the two types of induced draft cooling towers.

- The intimate exchange between water and air that can scrub contaminants out of the air
- Exchange of gases between the water and air
- Influx of fresh water, which is generally not treated to remove biological contaminants

All of these factors increase the challenges of effectively treating and controlling cooling tower systems. The first step in understanding the dynamic nature of cooling tower systems is to learn the calculations for the system dynamics.

Evaporative Condensers

Evaporative condensers are a special subset of wet evaporative cooling towers. An evaporative condenser is a small evaporative cooling tower with the heat exchanger inside the tower. Often, a serpentine coil is used for the heat exchanger. The coil contains a fluid to be cooled or condensed. Water cascades over the outside of the coil, providing evaporative cooling for the fluid within the coil. Evaporative condensers are commonly used in refrigeration, especially ammonia systems, and in some industrial cooling applications. The advantage of evaporative condensers is that cooling can be accomplished in a single step, without the need for additional heat exchangers or pumping the cooling water to the location of the heat exchanger.

Evaporative condensers can have a number of different designs. The air and water can travel in the same direction (parallel) or in opposite directions (counterflow). Air can be drawn (induced) or pushed (forced) over the coil by a fan. Some evaporative condensers, called combined units, have both a coil section and a separate fill section. In combined units, most of the evaporation occurs in the fill section and away from the coil, reducing the scaling and fouling potential for the coil. Examples of two designs are shown in Figs. 14.23 and 14.24.

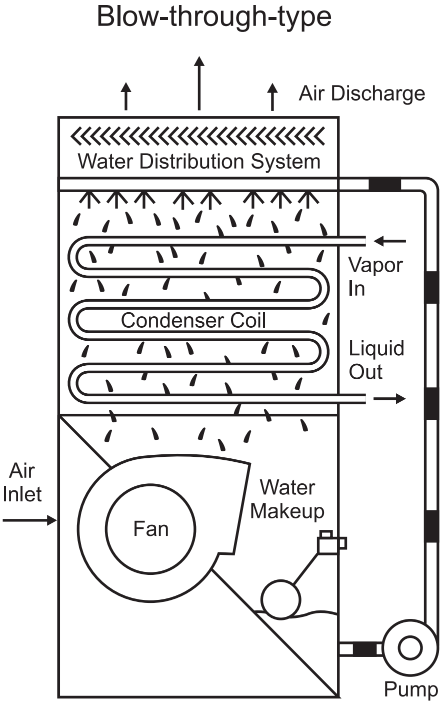


FIGURE 14.23 Blow-through-type evaporative condenser.

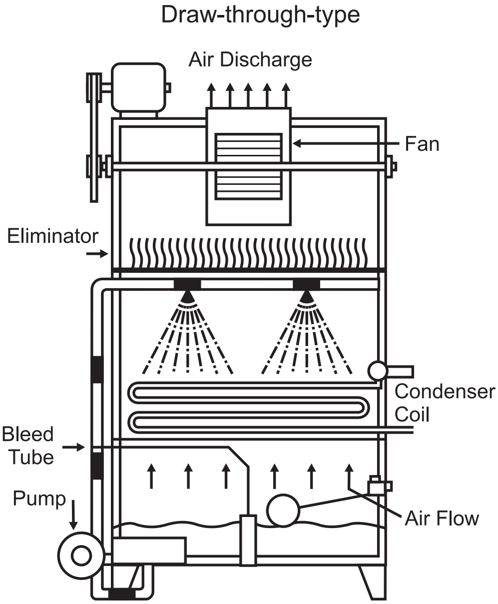


FIGURE 14.24 Draw-through-type of evaporative condenser.

Evaporative condensers experience the same problems as conventional open cooling tower systems with some notable additions. One of those problems is white rust from corrosion of galvanized components of the system. White rust is an unprotective deposit of zinc hydroxide or zinc carbonate on the surface of the metal. Evaporative condensers require thorough inspection of galvanized components. Any areas that show either total loss of the zinc coating or white rust should be noted. Both location and type of attack are important information. The presence of white rust can point to operation out of the desired control window of pH and alkalinity, or can point to improper passivation of a new or newly cleaned system. White rust is covered in more detail in Chap. 16 on Cooling System Corrosion.

Dry or Hybrid Tower Systems

The most widely used dry towers are commonly known as fin-fan coolers (Fig. 14.25). In most fin-fan coolers, the hot process liquid flows directly through the tubes, and air is blown over the outside of the tubes. These coolers do not use any cooling water.

Hybrid, or wet/dry, towers contain finned tubes in addition to normal cooling tower fill. In some of these towers, the hot, return water flows first through a set of tubes to reject heat without evaporation. The water then flows over normal cooling water fill to gain further cooling from evaporation. An example of this configuration can be seen in Fig. 14.26. In other configurations, the water can be diverted to flow either through the tubes or over the fill in the cooling tower. During colder weather, the cooling water is diverted through the tubes to provide nonevaporative cooling. During warmer periods, the water flows over the tower fill in an evaporative cooling mode.

Figure 14.25 A fin-fan cooler with two circular fans mounted under the bank of tubes that carries the hot process fluid. (*Courtesy of SPX Cooling Technologies, Inc.*)

Figure 14.26 A large combination wet-dry cooling tower used to cool condenser water at a utility station. (*Courtesy of the Public Service Company of New Mexico.*)

In either configuration, the tubes are susceptible to scaling, fouling, and corrosion.

Spray Ponds

Spray ponds are large basins or pits filled with water with a spray system located just above the water surface. The water inlet distribution systems are equipped with headers that contain spray nozzles. Through the nozzles, hot recirculating water is sprayed into the air where water is evaporated, cooling the remaining water. Because of the relatively short air-water contact time, heat transfer efficiency is limited. Windblown water loss in spray ponds is high, but can be reduced by a louvered fence on the downwind side of the pond. Because ponds are open to the atmosphere, the water can collect considerable quantities of foreign matter. Pumping costs are less for spray ponds than for cooling towers, because of lower head requirements.

Treatment programs for spray ponds are similar to those for conventional wet evaporative cooling towers, because all of the same conditions generally apply. Spray ponds are different from cooling lakes (covered earlier in this chapter), which are generally more like once-through systems.

Open Recirculating System Calculations

There are simple relationships between the makeup rate, blowdown rate, evaporation rate, and concentration cycles of a cooling tower or evaporative condenser. Other calculations can be more complicated, particularly if greater accuracy is desired. Often, measured makeup or blowdown rates are not available. In this case, determination of the recirculation rate and the temperature drop (ΔT) across the cooling tower can be used to calculate other necessary variables. The definitions and equations that follow illustrate the main calculations necessary to define the operation of a system.

Recirculation Rate (*R*) This is the flow of cooling water being pumped through the entire plant cooling loop, usually cooling a number of heat exchangers. Simply using the pump nameplate data to determine recirculating rate can be misleading. Throttling valves, pipe restrictions, and head pressure restrictions can produce significant deviations from the nameplate values. The actual recirculation rate is seldom more than the nameplate data and frequently may be 10 to 20% less. A pump curve, usually available from the manufacturer, is more accurate than nameplate data. A pump curve plots recirculating flow against pressure increase across the pump. By measuring the pressure increase, a reasonably accurate flow rate can be determined. A diagnostic study using special tracers is a preferred approach to accurately measure flow rate.

Temperature Differential or Range (ΔT) The temperature drop of the water passing through the tower is called the delta T (ΔT) or "range" of the cooling tower. Temperature drop is determined by the difference between the temperature of the hot return water to the tower (T_1) and the temperature of the cold water in the tower basin (T_2), as shown in Eq. (14.7).

$$\Delta T = T_1 - T_2 \tag{14.7}$$

The ΔT is used in several calculations, such as the approximation of evaporation rate of the tower.

Approach Temperature The efficiency of a cooling tower can be measured by how closely the cold water temperature in the tower basin "approaches" the ambient wet-bulb temperature. The approach temperature is the difference between the cold water temperature and the wet-bulb temperature. For economic reasons, water cooling towers are designed to have an approach temperature of 5 to 10°F (3–6°C), in other words, to cool the recirculating water to within 5 to 10°F (3–6°C) of the ambient wet-bulb temperature.

While water cooling towers work against the wet-bulb temperature, dry cooling towers work against the dry bulb temperature.

Evaporation Rate (*E*) Evaporation is the water lost to the atmosphere in the cooling process. The evaporation rate is dependent on the amount of water being cooled (R), the heat load (ΔT), and the ambient air conditions. Evaporation can be calculated using Eq. (14.8).

$$E = f(R)(\Delta T)(C_p)/\lambda \tag{14.8}$$

where E = evaporation, gpm (m^3/h)
f = evaporation factor, decimal value of the percent of heat rejection due to evaporation
R = recirculation rate, gpm (m^3/h)
ΔT = water temperature difference across the tower, °F (°C)
C_p = water specific heat, Btu/[lb · °F] (kJ/[kg · °C])
λ = water latent heat of evaporation, Btu/lb (kJ/kg)

The latent heat of evaporation for water at normal temperature and pressure is about 1000 Btu/lb (2300 kJ/kg). The specific heat of water is 1 Btu/[lb · °F] (4.1868 kJ/[kg · °C]) at normal temperature and pressure.

If all heat loss is only from the latent heat of evaporation, then $f = 1$ in Eq. (14.8). However, some sensible heat loss always occurs in cooling towers. Sensible heat loss (by conduction through the piping, etc.) can amount to as much as 20% of the heat loss of the system. Additionally, using $f = 1$ does not take into account the impact of varying relative humidity or ambient air temperature on the efficiency of the tower. Low ambient temperature can reduce evaporation simply by the cooling effect of the cold air in contact with the water. High ambient air temperature can increase evaporation because additional water evaporates to cool the air going through the tower. Low air humidity will increase evaporation, while high humidity will decrease evaporation. These factors affect the amount of evaporation, such that f can be as low as 0.5, indicating that only 50% of the heat rejection is due to evaporation.

Therefore, a general rule of thumb is that 85% of the heat rejection is due to evaporation ($f = 0.85$). This factor is applicable in most cases and will give a good approximation of the evaporation rate (E). Remember, this rule of thumb represents an approximation only, and some error is possible, particularly at low ambient air temperature or low and high humidity. Ideally, calculation based on a measured makeup or blowdown rate and the system concentration ratio is better.

Concentration Ratio (CR) The concentration ratio or cycles of concentration (COC) for any cooling tower can be calculated by dividing the concentration of any ion in the recirculating water (C_{BD}) by the concentration of the same ion in the makeup water (C_{MU}), as shown in Eq. (14.9).

$$\mathrm{CR} = C_{BD}/C_{MU} \tag{14.9}$$

Alternately, if flows are accurately known, the concentration ratio can be determined by dividing the makeup flow rate (MU) by the total blowdown (BD) flow rate, as shown in Eq. (14.10).

$$CR = MU/BD \tag{14.10}$$

The CR should be calculated for several individual components of the water to determine if the system is "in balance." In the ideal case, the system is in balance when the concentration ratios of all ions in the water (Ca, Mg, alkalinity, etc.) are equal (Table 14.3). Concentration ratios that are not equal can indicate that some mineral ($CaCO_3$, SiO_2, etc.) is precipitating from the recirculating water. For example, if the CR for calcium and alkalinity are more than 10% below the CR for magnesium, then $CaCO_3$ is probably precipitating in the cooling system. By knowing what may precipitate, the CR can be a valuable indicator that a problem is occurring.

The concentration ratios of some ions will be affected by chemicals added to the cooling system (Table 14.3). Acid for pH control, low or high pH products, bleach, chlorine gas, or other gases can affect both the alkalinity and CR of several ions in the cooling tower water. The CR for sulfate (SO_4^{-2}) would be increased when sulfuric acid (H_2SO_4) is added or where the plant atmosphere contains sulfur dioxide gas (SO_2). In these cases, the CR for alkalinity would be decreased, because alkalinity is destroyed by acid added to the tower. Chlorination of the cooling water will increase the CR for chloride (Cl^-).

The balance, of water evaporated, fresh makeup water added, and blowdown removed from the system, controls the concentration ratio. As CR increases from 1 to about 6, the amount of fresh makeup

Constituent (mg/L Except Conductivity)	**Makeup Water Corunna, Canada**	**Tower Water Corunna, Canada**	**Concentration Ratio**
Calcium ($CaCO_3$)	69	420	6.1
Magnesium ($CaCO_3$)	30	180	6
Sodium (Na)	7.7	77	10
Chloride (Cl)	13	100	7.7
Sulfate (SO_4)	19	510	27
M alkalinity ($CaCO_3$)	72	27	0.4
P alkalinity ($CaCO_3$)	<1	<1	—
Conductivity (μS/cm)	240	1400	5.8

TABLE 14.3 Example of Concentration Ratio Calculation from Tower and Makeup Water Analyses

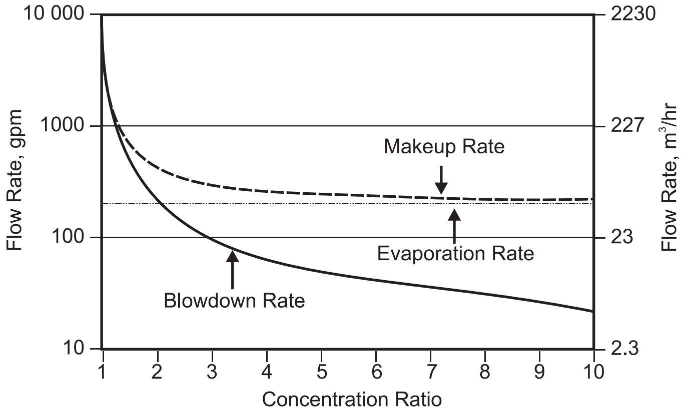


Figure 14.27 Reduction of makeup and blowdown rate as concentration ratio increases in a cooling tower.

water is reduced (Fig. 14.27). At values of CR above about 6, the reduction of makeup demand is smaller. The lower limit for the makeup rate is the evaporation rate.

Makeup (MU) Several expressions can be used to calculate the makeup rate. The simplest is the sum of the total system blowdown (BD) and evaporation rate (*E*).

$$\mathrm{MU} = \mathrm{BD} + E \tag{14.11}$$

The makeup rate can be calculated from total blowdown rate and the concentration ratio, if these two parameters are known.

$$\mathrm{MU} = (\mathrm{CR})(\mathrm{BD}) \tag{14.12}$$

If evaporation rate (*E*) and concentration ratio (CR) are known, the makeup rate can be calculated with Eq. (14.13).

$$\mathrm{MU} = (E)(\mathrm{CR})/(\mathrm{CR} - 1) \tag{14.13}$$

Blowdown (BD) Since pure water vapor is discharged by evaporation, the dissolved and suspended solids left behind concentrate. These solids would concentrate to brine, causing massive scale and corrosion, if there were no water loss other than evaporation. To balance this, controlled blowdown is discharged from the circulating system. Controlled blowdown (BD_C) is calculated to remove solids at the same rate at which the solids are introduced by the makeup. There are other uncontrolled losses from the system. One is drift (*D*) and the other is leakage (L), sometimes deliberate, but usually accidental. These are included in the total blowdown (BD) calculation.

$$\mathrm{BD} = \mathrm{BD}_C + D + L \tag{14.14}$$

The total blowdown is related to other parameters as shown in Eqs. (14.15) to (14.17).

$$\mathrm{BD} = \mathrm{MU} - E \tag{14.15}$$

$$\mathrm{BD} = \mathrm{MU}/\mathrm{CR} \tag{14.16}$$

$$\mathrm{BD} = E/(\mathrm{CR} - 1) \tag{14.17}$$

Drift (*D*) Cooling towers are designed with equipment to reduce drift, typically using mechanical drift eliminators, as shown in the previous figures. Drift consists of the fine droplets of water that escape from the tower through the drift eliminators in the plenum area of the tower. Drift is included in the determination of total blowdown (BD) above. However, an estimation of drift losses can be made if the drift eliminator efficiency factor is known. In recent years this efficiency factor has improved significantly from 0.005 to 0.02% to as low as 0.0005% of the recirculating rate (R). This value can generally be found in the cooling tower specifications. If the actual efficiency factor cannot be found, drift (D) would be calculated as shown in Eq. (14.18), using the approximation of 0.01% of R.

$$D = 0.0001(R) \tag{14.18}$$

Leakage (*L*) Circulating water may be lost in the plant through pump or valve leaks; by once-through cooling of pump glands, compressor jackets, or bearings; or such uses as equipment or floor cleaning, when the cooling water line happens to nearby. In some plants, large miscellaneous usage of recirculating cooling water prevents operation above a concentration ratio of 1.2 to 1.5. This severely limits the economical chemical treatment of the system and prevents effective conservation of water.

Holding Capacity or Volume (*V*) Usually, most of the water in a system is contained in the cooling tower basin or spray pond. An approximation of the holding capacity can be obtained by calculating the volume of water in the basin and adding an extra 20 to 30% for the water contained in the pipes and equipment. Additional increases may be required if the system has an unusually large number of open box condensers, jacketed vessels, or holding tanks. Because of variability in cooling systems, this estimate can be very inaccurate.

System volume can be determined most accurately with a diagnostic study using special tracers. This can provide the system volume, total blowdown rate, and the holding time index in the same study. A known amount of inert tracer is added to the cooling system. The controlled blowdown should be turned off, if possible. After the steady-state concentration of the traced compound in the cooling water is known, the system volume (V) can be determined. The blowdown is resumed and the traced material concentration is measured as a function of time. The blowdown rate, and hence the holding time index, can be calculated from the decay of the tracer concentration as a function of time.

Time/cycle (*t*) One cycle is defined as the time required for water to make one trip around the circulating loop. This time is a function of the holding capacity and the recirculation rate.

$$t = V/R \tag{14.19}$$

Holding Time Index Holding time index (HTI) is defined as the time required for the concentration of any ion to dilute to 50% of its original concentration in a cooling tower. HTI is essentially the "half-life" of a chemical added to a system. HTI is calculated from the system volume (V), the blowdown rate (BD), and the natural logarithm of 2 (0.693) with Eq. (14.20).

$$\text{HTI} = 0.693(V)/(\text{BD}) \tag{14.20}$$

Unique Problems of Cooling Tower Systems

Open recirculating systems can experience unique issues that are not encountered in closed and once-through cooling systems. Some examples follow.

Ambient Air Effects Cooling towers scrub the air passing through them to provide the evaporative conditions, handling about 120 to 240 ft^3 of air per gallon of water (900–1800 m^3 of air per cubic meter of water). The atmospheric environment around a tower can have profound effects on the thermal performance of the cooling tower system.

In some areas, the air contains large amounts of dust, as in arid sections of the world, especially where dust storms are common. Cooling systems in areas prone to this problem cannot work effectively without side-stream filtration. In a complex industrial plant, solids may become airborne from dirt on roads, open areas between plant buildings, or from open storage of solids (e.g., ore, coal, lime, or limestone). Any of these sources of particulates is as damaging as silt and requires side-stream filtration. Lime and limestone dust can dramatically affect cooling water scale control programs.

A more subtle, difficult problem is the presence of acidic or alkaline gases in the atmosphere. These gases affect the pH of the system, a critical control factor in any chemical treatment program that has a direct bearing on the scale-forming or corrosive tendencies of the water. An unusual, but pertinent, example is an ammonia plant cooling tower located between the ammonia process and the nitric acid process. When the wind is from one direction, ammonia in the atmosphere raises the pH of the system water. When the wind is from the opposite direction, acidic nitrogen oxide gases reduce the pH. Although this is an exaggerated case, this example illustrates that the pH of the system may be affected by the air around the tower.

Another example of gas entry into a cooling tower is when rooftop cooling towers are located too close to boiler exhaust stacks. This can allow carbon dioxide, carbon monoxide, and sulfur gasses to be dissolved into the cooling water.

The most prominent of the atmospheric gases are acidic, and chief among them is carbon dioxide (CO_2), which occurs at an average concentration of about 0.03% by volume in the atmosphere. The amount of CO_2 supported in water at about 68°F (20°C) by this partial pressure is less than 1 mg/L. However, the actual CO_2 level in a cooling tower system varies considerably from one plant to another because of local atmospheric conditions, such as the presence of industrial stack gas discharges.

There is a definite relationship between CO_2, alkalinity, and pH (see Chap. 4 on Water Chemistry). Because CO_2 is variable, predicting the alkalinity concentration at a specific pH value is difficult.

If the atmospheric CO_2 concentration is constant, then the relationship between alkalinity and pH can be defined. The pH will vary as a logarithmic function of alkalinity. The pH will increase by the log of 2, or a value of 0.3, if the alkalinity doubles. Similarly, if the atmospheric CO_2 doubles with a fixed alkalinity, the pH will be reduced by the log of 2 or 0.3 pH units. The expected equilibrium pH of any new system can only be established empirically, unless there is a record of previous experience near the new cooling tower or strong evidence that the average atmospheric CO_2 concentration is constant.

Fill Fouling Cooling towers are sometimes built with high-efficiency film fill instead of splash fill. High-efficiency fill provides greater cooling capacity with less volume, because water passages are closely packed together (Fig. 14.28). High-efficiency fill is much more prone to fouling with suspended solids and microbial contamination than splash fill (Fig. 14.29).

When fill fouling occurs, the fouling may be seen at the ends of the fill where water enters or leaves the fill. In some cases, scaling from hardness and alkalinity can cause severe fouling, as shown in Fig. 14.30. However, this is not always the case. High-efficiency fill is often prone to deposition about one-third of the way down from the top of the fill surface. This will be difficult to find, especially since there may be no evidence looking from the top or the bottom of the

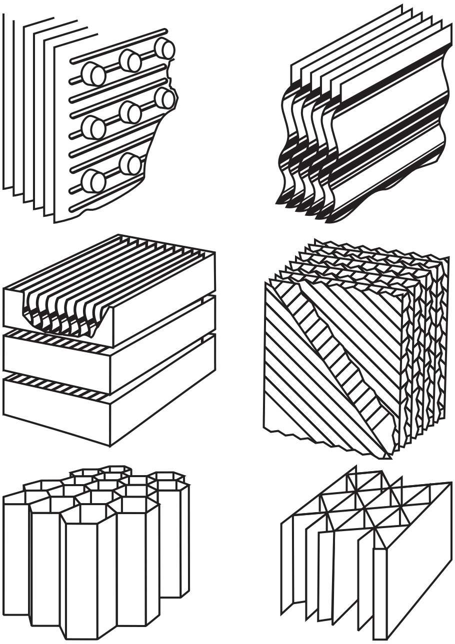


Figure 14.28 Diagram of several types of film fill, showing the variation in size of the passages for water and air.

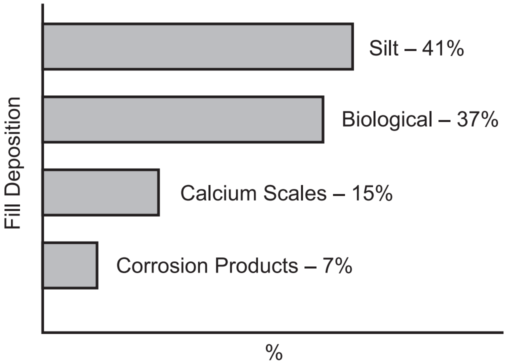


Figure 14.29 Average breakdown of cause of cooling tower fill deposits.

packing. Depending on the type of foulant on the fill, the material will range from white to brown or black. Scale deposits are generally white and may be either a continuous coating or spotty deposits that occur in wet-dry areas. Microbial deposits will vary in color depending on the organism. Suspended solids will often be gray or brown deposits.

Figure 14.30 Heavy fouling of film fill caused by inorganic scale formation.

Icing In some climates, either in the extreme northern or southern areas of the world, ice can form in any of the water-wetted areas of the cooling tower. This may occur particularly near the outside inlet for the cold air. The weight of ice on cooling tower components can cause significant damage. Icing on air intake louvers and packing next to louvers can restrict airflow or cause structural damage due to the weight of ice accumulation.

Wood Degradation Most tower lumber is either preservative treated or a rot-resistant species. Plastic components are often used in place of wood in newer towers. However, some towers have been constructed of cheaper, spruce wood, which has less natural resistance to biological attack. Wood can exhibit a variety of forms of attack in water-wetted systems:

1. Chemical surface attack or delignification is due to the selective removal of lignin from wood. Excessive chlorination at elevated pH for prolonged periods may cause this attack. Chemical surface attack is most prevalent in the flooded wood components or frequently wetted areas. Chemical

attack is a thin-layer surface attack and can be detected and controlled, if the attack is discovered before serious damage occurs. This form of surface attack is virtually nonexistent in the pH range of 6 to 8.

2. Iron rot is a chemical attack caused by the formation of iron salts around corroding ferrous parts in contact with wood. The wood in the adjacent zone has a charred appearance and may be more susceptible to fungal attack. Since connections are affected in many cases, extensive repairs may be required.
3. Biological surface attack (soft rot) is caused by fungi, which selectively attack cellulose of damp wood, leaving behind the lignin. This attack is characterized by a dark appearance, and the wood surface becomes soft and spongy or checked.
4. Biological internal attack occurs below the surface of the wood, and often goes undetected until the infection has spread widely, resulting in serious structural damage. The decay can be white rot, attacking both cellulose and lignin and leaving a spongy or stringy mass, or a brown rot, attacking primarily cellulose and leaving a brown cube-like pattern. This type of attack is more apt to occur in the warm, moist, but non-flooded portions of the tower.

The types of organisms that cause biological attack are covered in Chap. 17 on Cooling Water Biology.

Basin Sludge The presence of sludge in the cooling tower basin can cause problems throughout the cooling system. Basin sludge can be a source of microbial slime problems elsewhere in the cooling system, especially heat exchangers. Basin sludge can also harbor hazardous Legionella bacteria that can reinoculate the tower water if released from the sludge. (See Chap. 20 on Legionella and Legionellosis.) If the source of the sludge is either windblown dust and debris, or suspended solids in the makeup water, the cost of cleaning and additional dispersant may possibly help to justify the cost of side-stream filtration equipment. Often, a chlorination feed system that sweeps the total basin will have a beneficial effect on microbial control in the total system and help to minimize problems from sludge in the basin.

Intermittent Operations Some equipment, such as a chilled water system, often operates on a seasonal basis. Any system that is out of service can be a site of microbial growth. Stagnant water can also create severe corrosion problems. An out-of-service system should be monitored for microbial activity and inhibitor concentration maintained at proper levels. Periodic circulation is recommended.

Water Recycle Recycle or reuse of wastewater in cooling tower systems can offer economic and environmental benefits. These benefits generally come with added cost or risk to the system operation. Treatment programs may require modification to maintain low corrosion rates and clean heat transfer surfaces with the recycled water. Cooling tower systems are often considered the best candidate for use of recycled water, because of relatively lower water quality requirements and high usage rates. Even so, many potential problems exist. Increased dissolved solids in the wastewater can increase scaling or corrosion potentials. Organic contaminants in refinery and chemical plant wastewaters can cause fouling of system surfaces and increase microbial growth. Nutrient materials such as phosphate and ammonia can increase microbial growth. Depending on how the wastewater will be used, these contaminants must be removed or treatment programs modified to deal with these effects.

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CHAPTER 15

Cooling Water Deposition

Water is used in cooling systems because it is widely available in most industrial areas, is easy to handle, and has a high capacity to carry heat away from processes. Water is often called the universal solvent—a property that can cause unwanted side effects for industrial applications. Water can dissolve many substances. As a result, water can cause corrosion of metals used in cooling systems. Dissolved ions in the water may exceed the solubility of some minerals and cause scale formation. The life-giving properties of water can encourage bacterial growth that can foul system surfaces. Suspended solids in the water may deposit in low-flow areas and create unwanted fouling. These four problems (corrosion, scale, fouling, and microbial growth) require proper treatment and control to maintain the integrity and reliability of a cooling system.

For many years, Nalco has described the interrelated nature of these four cooling water problems in terms of a triangle (Fig. 15.1). The problems of corrosion, scale, fouling, and microbial growth do not happen in isolation. These problems can occur simultaneously, and each one can influence or even cause the other problems. The interrelated nature of the four problems is very important to understanding and controlling cooling system performance. A treatment program cannot address only one or two parts of the triangle, because another untreated issue can quickly cause any of the other problems. This is particularly true of biofouling, which can directly and indirectly cause corrosion, scale formation, and fouling by suspended material. Biofouling is at the center of the triangle because biological organisms can rapidly get out of control and swiftly increase the rate of any of the other three problems. The triangle is also a reminder that one of the central aspects of a good treatment program is effective microbial control. From a practical point of view, the four problems cannot be viewed individually, but must be addressed together in a complete program including proper treatment, system management, system control, and results monitoring.

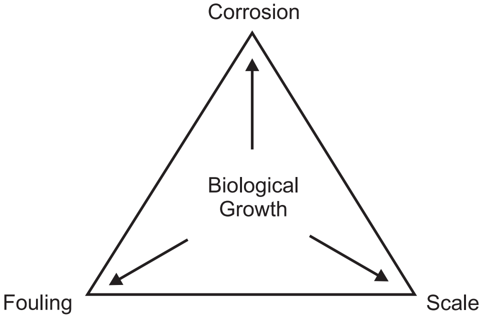

Figure 15.1 The problems in cooling water systems are closely interrelated, with biological growth as the central problem that can cause corrosion, scale, and fouling to occur or increase.

The need to look at all of the problems to identify the root cause can be illustrated by a simple case history. Exchanger performance monitoring showed that fouling was occurring in a cooling water system. This fouling reduced exchanger heat transfer efficiency and reduced overall system performance. A dispersant was added to the treatment program; however, the deposition continued. An analysis of the deposit was then obtained, showing that the fouling was mostly iron oxide from corrosion of the system. The corrosion inhibitor dosage was increased, along with the dispersant, but the fouling problem did not stop. A complete survey of the system showed that microbial growth was not effectively controlled and anaerobic corrosive bacteria were present in the system. These bacteria can directly influence corrosion rates in a cooling system. Improving oxidizing biocide control along with biodispersants to control the microbial problems in the system, reduced system corrosion and hence the iron fouling. This illustrates that biological growth is often the central problem in cooling water systems.

Even though the problems in cooling systems are interrelated, separate discussion and understanding of each of the four problems is necessary to obtain best results for cooling water system control. All treatment programs are made of individual components that address aspects of each problem. An understanding of the individual components is necessary to understand how the treatment programs function, and to select the correct program. Therefore, this section provides a basic understanding of corrosion, scale, fouling, and biological growth that occur in cooling water systems. Only in this manner can the best solution be chosen for complete treatment in any individual system.

Cooling system operation directly affects reliability, efficiency, and cost of any industrial, institutional, or power industry process. Maintaining control of corrosion, deposition, microbial growth, and system operation is essential to provide the optimum total cost of operation (TCO), as described in Chap. 14 on Cooling System Dynamics. Using computer optimization to select both an appropriate treatment program and optimum operating conditions to minimize system stresses is the first step. The next step is implementation of an appropriate monitoring program to evaluate system conditions and treatment program performance. The final step is the use of superior monitoring and control technology to control system stress, optimize operating conditions, and control program parameters to minimize TCO.

Consequences of Deposition

Scaling and fouling can be separate processes but are often considered the same problem. The terminology is such that both words can be used to describe similar or separate aspects of deposition. In this book, deposition is considered the overall process that includes scaling and fouling. Scaling is a chemical process involving precipitation of insoluble compounds, whereas fouling is predominantly a physical process involving the settling of suspended particles. Scaling and fouling are related because each problem can aggravate the other. The two processes are described separately, but scaling and fouling generally happen together, and a complete treatment program must address both problems.

As deposits grow, water flow rate decreases and pumping backpressure increases. The deposits have lower thermal conductivity than the metal heat exchange surfaces, causing reduced heat transfer. Deposition results in decreased plant efficiency, reduced productivity, schedule delays, increased energy costs, loss of production from downtime for maintenance, and increased costs for equipment repair and replacement. All of these effects directly lead to higher operating costs and decreased profitability. Deposition also has a capital cost penalty, because heat exchangers are commonly built about 15% larger to accommodate the normal fouling that will occur.

Common types of deposition in cooling systems are:

- Mineral scale—precipitation of insoluble compounds from ions in the water
- Suspended material—insoluble material that can settle in low flow areas
- Corrosion products—deposits that result from insoluble materials formed by corrosion
- Process leaks—typically organic foulants introduced from the process being cooled
- Microbial deposits—created by the action or growth of microorganisms

The component elements of a deposit are typically determined by X-ray fluorescence (XRF). This technique identifies the elements present by measuring the characteristic X-rays released by an element, when the sample is irradiated by an X-ray source. The compounds that may be present in the deposit are determined by X-ray diffraction (XRD). The sample is irradiated with an X-ray beam, and the diffraction pattern that results is analyzed. Crystalline materials produce a diffraction pattern that is unique for each mineral present. XRD can differentiate between crystalline and amorphous (noncrystalline) deposits, but cannot identify the composition of amorphous materials.

Table 15.1 shows examples of deposit analyses containing typical cooling system deposits from a variety of locations in different cooling tower systems. Deposits of primarily calcium carbonate are common and can be found in various areas of the system (Samples 2, 3, and 4). Calcium sulfate is less common, but can be found in the tower fill or heat exchangers, depending on the form of calcium sulfate that occurs (Sample 1). Iron oxide is found most often in system piping and exchangers but may be transported through the system to the deck of a cooling tower (Sample 5). Sample 6 is an example of organic fouling that may have come from a process leak.

Scale is one of the most common problems encountered in cooling water systems. Scale is the precipitation of minerals resulting when the concentration of ions in solution exceeds the mineral solubility. Scale generally forms hard and adherent layers, which retards heat transfer. Scale in transfer pipes can reduce water throughput, which can accelerate fouling further. Scale formation generally needs a temperature gradient, but can occur without a temperature differential in some conditions. Scale can also form in the cooling tower fill, where the ions in the water concentrate by evaporation.

Fouling is distinguished from scaling in that fouling deposits are formed from material suspended in water. Fouling is the aggregation of insoluble material through physical processes. Materials that cause fouling include suspended solids, organic contaminants like oil, corrosion products, and microbial growth. The combination of these problems complicates the fouling mechanism and is the reason that fouling is difficult to prevent. Fouling can occur without a temperature difference in any part of a cooling system, including cooling tower deck, basins, and fill.

In general, deposition will occur due to variation of environmental factors such as an increase of suspended solids in the makeup water, lack of control of cooling system parameters such as concentration ratio, or due to misapplication of treatment programs. This chapter will cover the scale formation process and fouling from insoluble material. Examples of common deposits found in cooling water systems will be covered. Microbial fouling will be covered in a separate chapter.

Sample Number	1	2	3	4	5	6
Source of Deposit	**Tower Fill #1**	**Heat Exchanger**	**Tower Fill #2**	**Tower Basin**	**Tower Deck**	**Cooling Tower**
			XRF Elemental Analysis*			
Aluminum as Al_2O_3				1%		
Copper as CuO					1%	2%
Calcium as CaO	30%	49%	49%	45%	1%	1%
Iron as Fe_2O_3		2%		1%	86%	
Fluoride as F		1%				
Magnesium as MgO	1%	2%	1%	1%	1%	
Manganese as MnO_2					1%	
Phosphorus as P_2O_5	1%	5%	1%	1%	2%	1%
Silicon as SiO_2	9%	2%	2%	9%	3%	
Sulfur as SO_3	38%	1%	2%	1%		
Zinc as ZnO	4%			1%	1%	
Loss at 925°C†	17%	38%	45%	40%	4%	96%
Total	100%	100%	100%	100%	100%	100%

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*The results for the X-ray fluorescence (XRF) analysis were normalized to loss at 925°C, such that XRF + L925 = 100%.

†The loss at 925°C includes water of hydration, CH_2Cl_2 extractables, all organics (carbon, hydrogen, nitrogen), many sulfur compounds, the CO_2 from most carbonates, and some volatile compounds.

TABLE 15.1 Analyses of Cooling System Deposits That Contain Mineral Scale, Suspended Solids, Corrosion Products, and Organic Foulants

Sample Number	**1**	**2**	**3**	**4**	**5**	**6**
Source of Deposit	**Tower Fill #1**	**Heat Exchanger**	**Tower Fill #2**	**Tower Basin**	**Tower Deck**	**Cooling Tower**
Other Analyses						
CH_2CH_2 extractible	Not detected	Not detected	Not detected	<1%	Not detected	65%
Carbonate as CO_2	4%	33%	36%	30%	Not detected	Not detected
Most Probable Composition	Calcium sulfate	Calcium carbonate	Calcium carbonate	Calcium carbonate	Iron oxide	Organic matter
	Calcium carbonate	Calcium phosphate		Silica		Spot test indicates bacteria
	Silica					

Table 15.1 Analyses of Cooling System Deposits That Contain Mineral Scale, Suspended Solids, Corrosion Products, and Organic Foulants (*Continued*)

The Scale Formation Process

Scale forms when crystals of an insoluble mineral grow on surfaces in cooling systems. In some cases, precipitation can occur in the bulk solution, and scale then forms by an agglomeration of suspended scale particles, which deposit on surfaces in a fouling process. Scale can be crystalline or amorphous in nature. Amorphous refers to the lack of an ordered or crystalline structure. Understanding the conditions for scale formation and which factors affect the solubility of a mineral, will help to understand how to control this part of the deposition process.

For scale to occur, the right conditions for scale formation must exist. These conditions include:

- Saturation of the component ions of the mineral
- Nucleation sites—for example, rough metal surfaces or small particles of scale
- Contact time to allow the growth of scale crystals
- Scale formation rate exceeding the dissolution rate
- Strength and hardness of the scale is sufficient to resist the shear forces of flowing water

Scale formation may occur when ions of a given mineral in the cooling water concentrate above the solubility of that mineral. Scale can form anywhere in the system in combination with corrosion, fouling by suspended material, or with biofouling. The presence of suspended solids, corrosion products, corrosion sites, welds, crevices, surface roughness, oxide films, and evaporation over the tower fill can initiate seed scaling.

Solubility Is an Equilibrium Process

Generally, minerals that can precipitate in cooling systems are ionic solids. When a solid dissolves in water, the ions that form the compound are released into solution. Even when sparingly soluble minerals like calcium carbonate ($CaCO_3$) are added to distilled water, the mineral will dissolve as shown in Eq. (15.1):

$$CaCO_3 \rightarrow Ca^{+2} + CO_3^{-2} \tag{15.1}$$

When the salt is first added, the ions dissolve rapidly. As more salt is added, the concentrations of the ions soon become large enough that the reverse reaction (precipitation) starts to compete with dissolution. Eventually, the calcium (Ca^{+2}) and carbonate (CO_3^{-2}) ion concentrations become large enough in the solution that the rate of precipitation equals the rate at which $CaCO_3$ dissolves. Once that happens, there is no net change in the concentration of these ions with time, and the reaction is at equilibrium. When the system reaches equilibrium, the solution is called a saturated solution, because the liquid contains the maximum concentration of ions that can exist in equilibrium with the solid salt. The equilibrium is represented in Eq. (15.2):

$$CaCO_3 \rightleftharpoons Ca^{+2} + CO_3^{-2} \tag{15.2}$$

The amount of salt that must be added to a given volume of solvent to form a saturated solution is the solubility limit of the salt, and defines the saturation ratio (SR) or saturation index (SI) at a given set of conditions (temperature, pH, ionic strength, etc.). At equilibrium, the SR or SI equals 1.0. A supersaturated solution exists when the concentration of the ions is higher than the equilibrium levels ($SR > 1$). In this case, the rate of precipitation may increase. If the concentration of ions drops below the equilibrium levels ($SR < 1$), solubility increases, and precipitation will stop. A cooling tower system can reach $CaCO_3$ saturation very quickly. When the conditions of water chemistry, pH, and temperature exceed the solubility limit, $CaCO_3$ precipitation can occur.

Nucleation and Scale Formation

In a cooling water system, scale can appear rapidly, and grow to visible thick layers in a short time. Although the growth of scale can seem very simple, the process of scale formation is a series of steps as illustrated in Fig. 15.2. First, water with dissolved minerals must be concentrated so that the ions of a given mineral are above the solubility of that mineral (supersaturation). Crystallization of scale will only occur if some degree of supersaturation exists. The degree of supersaturation is a prime factor for controlling the deposition process. Once supersaturated, there is typically an induction period before nucleation occurs. The induction period is defined, as the time required from the point of supersaturation to the initial formation of small particles of mineral scale.

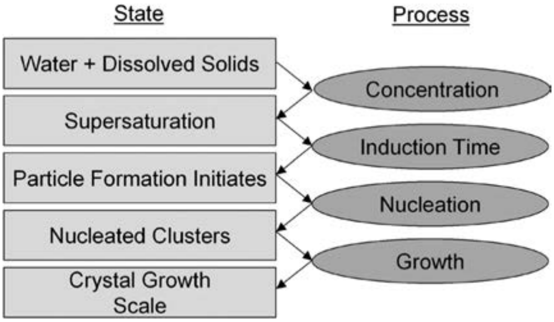

FIGURE 15.2 The steps that lead to scale formation.

A supersaturated solution will not form scale unless some solid sites exist where crystals can grow. These sites may be seed crystals of the mineral, suspended solids particles, rough metal surfaces, or microbial deposits. The formation of many small particles that act as sites for additional crystal growth is called nucleation. This nucleation process can follow two different paths, either occurring spontaneously or induced by external forces.

Homogeneous versus Heterogeneous Nucleation

Nucleation occurs by two basic mechanisms: homogeneous and heterogeneous nucleation. Homogeneous nucleation occurs spontaneously (self-seeding) and can be caused by a high degree of supersaturation of the scaling ions. Heterogeneous nucleation occurs when foreign particles or irregularities on system surfaces seed scale formation. Heterogeneous nucleation is more common in cooling water systems, due to the presence of suspended solids, microbial deposits, corrosion products, corrosion sites, welds, crevices, surface roughness, and oxide films, all of which can initiate nucleation or seed the formation of scale.

For homogeneous nucleation to occur, a minimum number of molecules (in the thousands) must orient themselves into a fixed lattice. If nuclei are too small, these nuclei will redissolve. The nuclei become stable after exceeding a certain size (above a critical radius). The time required for nucleation varies, depending largely on the degree of supersaturation. The time required for nucleation decreases as supersaturation increases.

In reality, homogeneous nucleation is a difficult process. The molecules in solution must collide, not redissolve, orient themselves into a fixed crystal lattice, and additional molecules must add to the surface to continue the scale formation process. Many of these initial clusters of scale molecules must be present to form a noticeable amount of scale. The solution must remain supersaturated so that the process continues.

When nucleation begins, several processes are possible:

- The nucleated particles can redissolve, if the level of supersaturation is not sufficiently high or if an inhibitor is present.
- The nucleated clusters can form on solid surfaces in the system and grow into layers of scale.
- The nucleated clusters can form in the bulk solution, if the level of supersaturation is very high.
- If nucleated clusters form in solution, the process of agglomeration to form scale may be balanced by dispersion to keep the particles separated and floating in the water.

The formation of stable nucleated clusters depends on the free energy of the molecules in solution, compared to the free energy

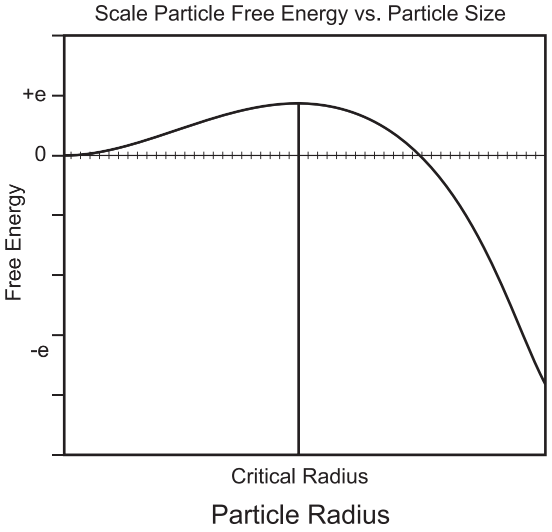

Figure 15.3 The behavior of new nucleated clusters depends on the particle size. The nucleated cluster can grow or dissolve, whichever results in a decrease of free energy of the system.

released when the solid is formed. Homogeneous nucleation first requires energy to bring the molecules together. The energy required is related to the degree of supersaturation, such that a highly supersaturated solution requires less energy for spontaneous nucleation. Energy is required to form nucleated clusters up to a certain critical radius (Fig. 15.3). Above this critical particle size, energy is released by the formation of the solid. As crystal growth continues, the free energy released by the solid is greater than that required to form the nucleated clusters, and scaling continues.[1]

In heterogeneous nucleation, the presence of impurities or foreign material in solution can significantly affect the rate of nucleation. Inhibitors can slow the scale formation process. Suspended solids, microbial growth, corrosion products on surfaces, and rough metal surfaces in cooling systems, can increase the formation of nucleated clusters of scaling minerals. These impurities stimulate the scale formation process by reducing the energy required to form the nucleated clusters of scale molecules, or reduce the level of supersaturation needed to start the nucleating process. The free energy change of formation of the crystal nuclei by heterogeneous nucleation is lower than the energy change required for homogeneous nucleation.

At this point, the scaling process can go either way, because the growth of scale depends on the size of the particles and energy of

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[1] This phenomenon is discussed in greater depth in Mullins, J. W., *Crystallisation*, London: Butterworth and Company, Limited, 1972, pages 136-150.

the system. If the energy is not sufficient to reach the critical size, the nucleated clusters will redissolve. If enough energy is present, the nucleated clusters will reach the critical size, continue to grow, and scale will form. One role of scale inhibitors can be explained during this nucleation process. The inhibitor can be adsorbed onto growing nucleated clusters and prevent them from reaching the critical size. The nucleated clusters will then redissolve and release the inhibitor back into solution. In well-inhibited and controlled systems, this illustrates why the inhibitor is not consumed while preventing scale formation. However, if the system is not controlled properly, the nucleated cluster will continue to grow past the critical size. These growing scale clusters will consume any adsorbed scale inhibitor. Monitoring this process of inhibitor consumption can be used to measure scaling stress in a cooling system. This is covered in more detail in Chap. 19 on cooling water treatment and control.

Crystal Formation

This is the beginning of a fixed crystal lattice. The lattice may form layers that allow growth to continue by adding individual scale molecules. The continued growth into crystalline scale is dependent on a variety of factors:

- Degree of supersaturation
- Temperature
- pH of the water
- Presence of impurities or seed crystals
- Concentration of dissolved carbon dioxide (CO_2) will affect nucleation of calcium carbonate
- Flow velocity of the water

Once nucleation has formed stable particles, larger than the critical size, visible scale crystals will grow. These growing crystals generally spread outward in a layer (called a terrace) as shown in Fig. 15.4. Each layer is only one molecule thick, and may have other seed clusters growing on top of the layer (forming steps). If solution conditions are right, the growth will continue as new molecules continually adsorb onto the growing steps or form new clusters. Scale inhibitors can affect either the formation of the initial molecule clusters or the growing crystal steps.

Crystals have distinct configurations, in which individual molecules are oriented into precise crystal structures. The specific form of crystal that grows, depends on the solution conditions and rate of scale formation. If precipitation is rapid, the scale molecules may simply adsorb in any orientation, forming an amorphous deposit. Impurities may adsorb onto the scale surface, which changes the direction of the growing layer. Whether the crystals grow in a defined

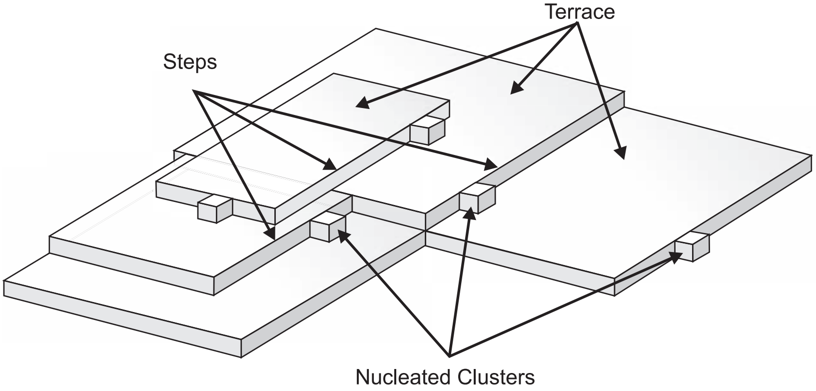


Figure 15.4 Crystal growth occurs in layers with new crystals forming along the edges of each terrace.

lattice, in misaligned layers, or in an amorphous mass, depends on the type of mineral, its properties, the supersaturation level, pH, temperature, impurities in the solution, and the presence of scale inhibitors.

Kinetic versus Thermodynamic Factors

The solution will try to maintain the lowest energy, whenever possible. The precipitation of a solid scale may be a lower energy state, than having the same ions dissolved in the solution. This is the thermodynamic consideration of scaling. On the other hand, some minerals take a very long time to form, even if the energy of the solid scale is less than that of the solution. The rate of formation is the kinetic aspect of scale formation. The difference between the thermodynamic and kinetic factors can be seen in the following simple example. Quartz has a much lower solubility than amorphous silica, but the rate of formation of quartz is so slow that quartz will not occur in a cooling system. This may not seem important to the operator who has silica scale in a tower, but this difference is essential to the understanding and inhibition of any mineral scale. With this knowledge, system conditions can be controlled to minimize the energy driving forces for precipitation, and inhibitors can affect the kinetic rate of scale formation and growth.

Phase Transitions

Scale that precipitates rapidly often forms a relatively porous structure that is easily removed with little mechanical effort. However, aging can change the physical characteristics of most scale deposits. Scale tends to harden and becomes more dense during aging. Older scale deposits are more adherent and difficult to remove. The aging phenomenon is due to dissolution, redeposition, and regrowth of crystals, or to phase changes involving hydration or dehydration. These aging processes can cause the individual crystals to become a solid, unified mass. Aging of scale is accelerated on heat transfer surfaces.

Adherence

A primary factor influencing scale adherence is surface roughness. Consequently, adherent scale forms more readily on corroding surfaces than on noncorroding surfaces. In addition, corrosion by-products tend to mix with forming scales and thereby increase adhesion of the mixture. Easily corroded metals result in significantly more deposits (mixtures of scale and corrosion products) than metals that do not corrode. When an alloyed metal surface is very smooth, scale deposition is lower than on a rough surface. Thus, microscopic surface roughness, whether naturally present or produced by corrosion, tends to increase the adherence of scale deposits.

Factors Affecting Scale Formation

Cooling water chemistry, operating parameters, and basic system design factors affect scale formation. These include but are not limited to the following:

- Concentration—The buildup of sparingly soluble compounds due to evaporation by a cooling tower.
- pH shifts—Stripping of CO_2 from carbonate buffered water causes the pH to increase.
- Process leakage—Can cause fouling and increase pH, making many scale-forming minerals less soluble.
- Temperature—The skin temperature of heat transfer surfaces can significantly affect scale formation of some minerals.
- Corrosion control—Cathodic corrosion inhibitors like phosphate or zinc can contribute to scaling when misapplied. This can result in precipitation of calcium phosphate or zinc compounds.
- Water quality—The presence of microbial growth or suspended solids in the water can increase deposition potential.
- Operational variability—Poor control of cooling tower water concentration ratio, changes in makeup water composition, and poor control of inhibitor dosage can result in scale formation.
- Misapplication of inhibitor programs—Over dosage of some inhibitors can cause scale.

Solubility factors affect the equilibrium process and the potential for scale formation. Any mineral in solution is affected by the total composition and conditions of the solution. Some of the factors that influence scale formation should be understood in more depth.

Common Ion Effect

The concentrations of ions in solution are affected by all equilibria and all ions present in the solution. The simplest and most significant effect is called the common ion effect, which occurs when an ion comes from two different salts in solution. For example, if sodium carbonate (Na_2CO_3) is added to water saturated in $CaCO_3$, the increased concentration of CO_3^{-2} will shift the equilibrium to cause $CaCO_3$ precipitation.

The Role of Temperature

Most compounds are more soluble in water as temperature increases. This is called normal or direct solubility. Scaling materials such as gypsum ($CaSO_4 \cdot 2H_2O$) and silica (SiO_2) have normal solubility. Under conditions of supersaturation, these materials may selectively form scale in cooler parts of a system, such as tower basins or fill. However, many of the common scale-forming minerals have inverse temperature solubility, which means that the solubility of these minerals decreases with an increase in temperature (Fig. 15.5). Calcium carbonate and calcium phosphate are inversely soluble and precipitate where temperature is highest. Thus, high skin temperature can lead to localized scaling of the heat exchanger surfaces, which reduces heat transfer.

As a result, the solubility of potential scaling minerals will be different in different parts of the system (Fig. 15.6). Scale control is important throughout the entire system. Deposition can reduce the

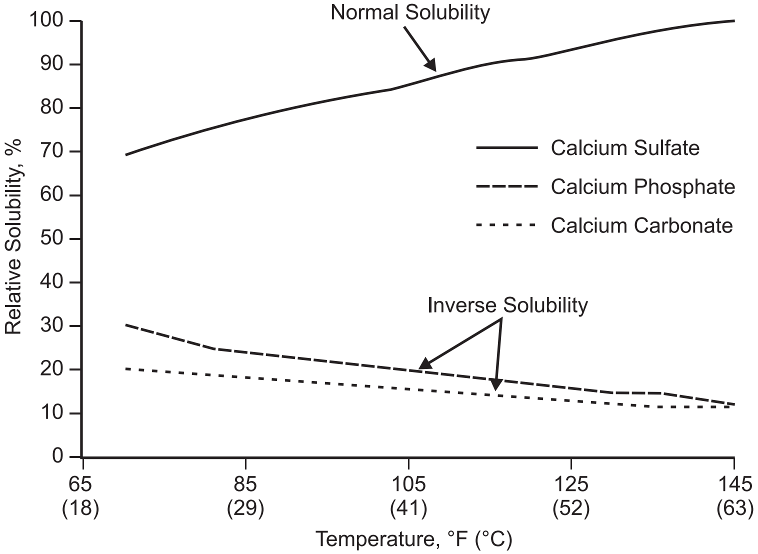


FIGURE 15.5 Example of how temperature affects the solubility of directly and inversely soluble compounds.

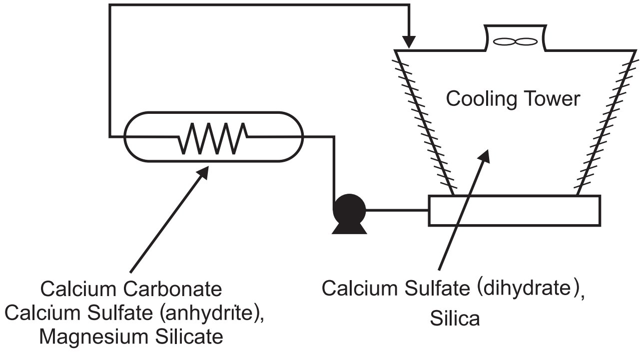


Figure 15.6 Minerals that are insoluble at high temperature (inversely soluble) may precipitate in heat exchangers, while minerals that are insoluble at low temperature (directly soluble) may precipitate in the cooling tower fill.

efficiency of either the heat transfer process in exchangers, or water and air flow in the cooling tower. Either effect can have a negative impact on process efficiency.

Ionic Strength and Particulate Material

High total dissolved solids (TDS) caused by ions that do not precipitate (e.g., sodium, potassium, and chloride) can extend the solubility of some scaling salts such as calcium sulfate ($CaSO_4$). Systems that have high TDS will benefit most from this effect (Fig. 15.7). On the other hand, high suspended solids increase scale potential primarily by increasing the number of nucleation sites where scale crystals can form.

Ion Pairing

Certain ions form a soluble ion pair that will decrease the deposition potential of other scale-forming salts. For example, $CaCO_3$ will have a given solubility by itself in water. When magnesium chloride ($MgCl_2$) is added, the solubility of Ca^{+2} is increased, due to the formation of more soluble magnesium carbonate ($MgCO_3$) and magnesium bicarbonate ($Mg(HCO_3)_2$) ion pairs in solution. The ion pair is a weak association of the two ions, but this pairing can have a positive effect (Fig. 15.8). This effect is the opposite of the common ion effect mentioned earlier.

Effect of System pH

System pH has a significant effect on scale deposition in cooling water systems. As pH increases, so does the scaling potential for most common scales in cooling water, including calcium carbonate, calcium and zinc phosphates, zinc hydroxide, and magnesium silicate. Low pH excursions accelerate corrosion, thereby producing soluble corrosion products, which can directly or indirectly promote scale formation.

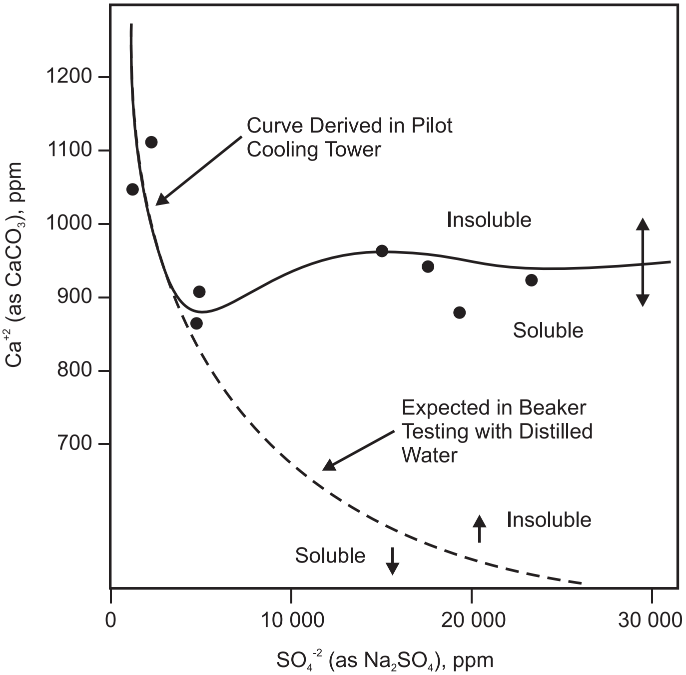


Figure 15.7 Example of how high conductivity can increase solubility of a scaling mineral like calcium sulfate.

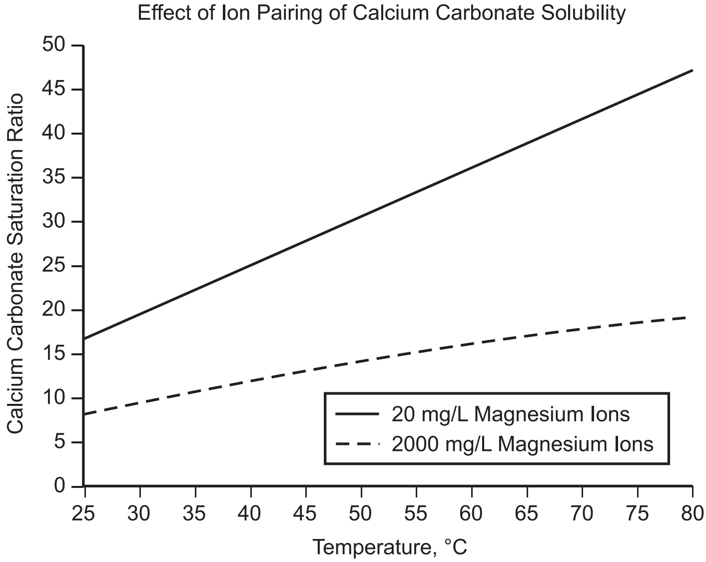


Figure 15.8 Illustration of how magnesium carbonate ion pairs can increase calcium carbonate solubility.

In cooling towers, the contact between air and water in the tower will strip CO_2 from carbonate buffered water, causing the pH to increase. This also changes the balance of bicarbonate (HCO_3^-) and carbonate (CO_3^{-2}) alkalinity. If concentration ratio and pH are not controlled, this shift in alkalinity caused by the stripping of CO_2 can lead to scale formation.

Flow Velocity and Hydrodynamics

Low water flow velocity [<2 ft/s (0.6 m/s)] in heat exchanger tubes can result in nonturbulent or laminar flow. This creates a very low velocity boundary layer of water next to the metal surface. This phenomenon results in less efficient convective heat transfer and produces higher surface temperatures. The extent of scale formation depends on the steady-state balance between scale-forming processes such as surface precipitation or particle agglomeration, and scale removal processes such as removal by shearing or sloughing. The rate of removal by flow shear directly depends on flow velocity.

Coprecipitation

Coprecipitation is the capture of an ordinarily soluble mineral with a scale that is precipitating. An example is the precipitation of silica with calcium carbonate, magnesium hydroxide, zinc hydroxide, or ferric hydroxide, when silica is present below the level at which precipitation of SiO_2 would be expected. Another example is the precipitation of phosphates on precipitating iron hydroxide floc.

Predicting Scale Formation

A variety of empirical and theoretical scaling index calculations have been used to predict the probability of mineral scale formation. Early methods of predicting the scale-forming tendency of water, range from simple equilibrium saturation indices, to empirical indices based on experimental or field data. The two key examples of these are the Langelier and Ryznar indices.

Langelier Saturation Index

This was the first index to come into wide usage (1920s). This index is based on the saturation pH (pH_S) of $CaCO_3$ in water. The definition of the pH_S is the pH at which a given water is saturated with calcium carbonate. The first step is to calculate the pH_S of the water. Then determine the Langelier saturation index (LSI) by the difference between the actual pH and the saturation pH for $CaCO_3$, as shown in Eq. (15.3):

$$\mathrm{LSI} = \mathrm{pH} - \mathrm{pH}_S \qquad (15.3)$$

$$\mathrm{LSI} > 0 \Rightarrow \text{Scaling}$$

$$\mathrm{LSI} \leq 0 \Rightarrow \text{Non-scaling}$$

As Langelier noted, the index is an indication of driving force and not a quantitative indication of scale formation.

Ryznar Stability Index

The LSI gives equal weight to pH and the dissolved solids content. This index is more predictive of the saturation state than the amount or severity of potential deposits. Ryznar (1938) developed a correlation between actual reported problems in the field with water chemistry, defining a new, empirical index shown in Eq. (15.4):

$$\mathrm{RSI} = 2\mathrm{pH}_S - \mathrm{pH} \tag{15.4}$$

$$\mathrm{RSI} > 6.0 \Rightarrow \text{Corrosive}$$

$$\mathrm{RSI} < 6.0 \Rightarrow \text{Scaling}$$

Ryznar Stability Index (RSI) gives more weight to the dissolved solids content of water than to the saturation state, so RSI should be more predictive than LSI of the severity of problems.

These first indices were an attempt to define the effect of water chemistry on scaling and corrosion. Both LSI and RSI were originally developed to enable better control of calcium and alkalinity adjustments in municipal water systems. Both are based on calculations of the solubility of calcium carbonate within limited ranges of temperature and dissolved solids. Both LSI and RSI assume that water supersaturated in $CaCO_3$ will form scale. The RSI assumes that below saturation, water is corrosive to iron. While water that is supersaturated in $CaCO_3$ may be scale forming, water that is subsaturated with respect to $CaCO_3$ may not be corrosive. Many similar indices are available for minerals such as calcium sulfate, calcium phosphate, magnesium hydroxide, and silica. Examples include the Stiff/Davies Saturation Index, the Larson and Buswell Index, and the Larson/Skold Corrosivity Index.

All indices are either inherently or intentionally limited in scope to make them easy to use. None of these methods considers all the complex factors in natural water that affect mineral solubility. In cooling tower applications, the inherent limitations of these simplified indices can give erroneous predictions of the scaling or corrosive tendency of the water. These limitations include:

- The effects of temperature and ionic strength are either ignored or severely limited.
- The solubility of other scaling species (besides $CaCO_3$) is ignored.
- The effects of soluble complexes (ion pairing) are not calculated.
- For new systems, a predicted pH based on the concentrated makeup water must be used, which is often in error.

- Simplifying assumptions are made about the carbonate equilibrium.

Simple indices are at best, rules of thumb, and should seldom be applied to cooling tower systems, even though from a practical view, indices are very easy to calculate and interpret. Today, the availability of computers and software that can consider the complex equilibria that occur in cooling systems makes simple indices obsolete.

Capabilities of Computer Models

The limitations of simple indices are not due to a lack of understanding of the problem, but to efforts to simplify the equations for general use. However, with the computer, rigorous calculations can be done much more easily and quickly. The effect of a wide variety of conditions, such as temperature, pH, ionic strength, common ion effects, ion pairing, and various inhibitors, can be determined rapidly and easily using a computer model. With these methods, a profile of the scaling tendency of the makeup water for a cooling tower, can be readily determined. With empirical correlations, accurate predictions of the corrosion rate provided by various treatment programs can also be obtained.

Accurate temperature adjustments to equilibrium constants and compensation for ionic strength effects can be calculated. The models can include large databases of soluble and solid/solution equilibrium constants. Also important are the calculation of the effect of soluble complexes, where ion pairing can increase the solubility of other less soluble minerals.

The real benefit of computer models comes from the predictive ability of this software. These models can predict the impact of changes in operating cooling systems as the water concentrates and equilibrates with the air. This can include calculation of the pH that will result in a system under various conditions, based on the effect of soluble gases and calculation of the CO_2 equilibrium in a system. For scaling systems, a calculation of the amount of potential deposits can be performed. Incorporation of oxidation/reduction equilibria allows the prediction of corrosion potentials as well. Empirical correlation of the effect of water chemistry on corrosion can enhance the oxidation/reduction equilibria calculations to provide better accuracy.

Some models have been adapted to water treatment use by addition of information on the performance of treatment chemicals. For example, the effect of deposit control chemicals on equilibrium behavior of potential mineral scale can be predicted. This is valuable with sparingly soluble inhibitors such as phosphate and zinc, where the solubility behavior of inhibitor components can be modeled. Finally, the capability to graphically compare the effect of operational parameter changes on water chemistry allows "what-if" scenarios to

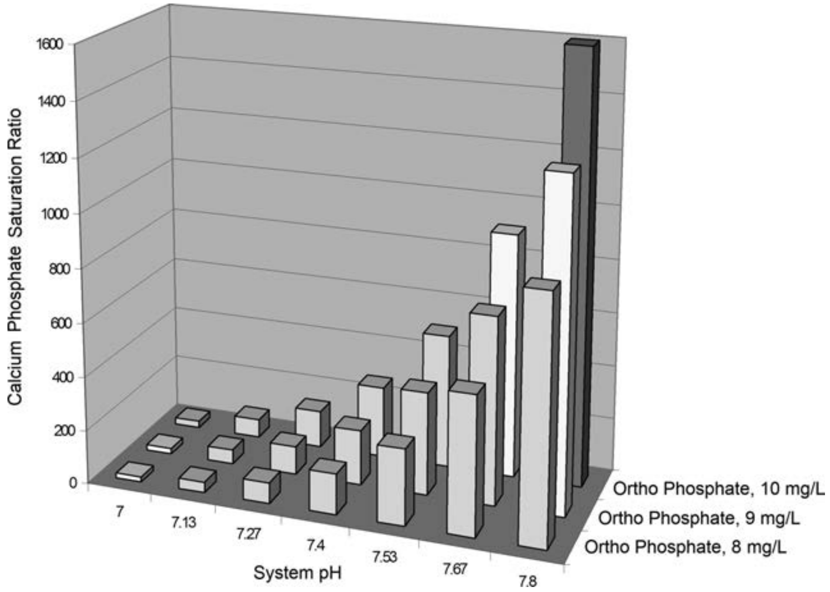


Figure 15.9 Sophisticated computer models can quickly evaluate solubility over a wide range of conditions and consider complicated ionic interactions in solution, including inhibitor effects. In this graph, higher saturation ratio indicates lower solubility of calcium phosphate.

be evaluated safely, without experimentation on an operating system. The clear advantage of computer models over simple indices is obvious (Fig. 15.9).

Fouling Deposition

Fouling is the aggregation and settling of insoluble material suspended in water through physical processes. Fouling can be caused by a variety of sources:

- Suspended solids—Scrubbed into cooling towers through contact with air or from turbid makeup sources. Road dust, suspended silt, and clay deposits are commonly seen.
- Organic contamination—Contamination of tower water by process fluids that leak into the water results in organic fouling. Oil fouling in refinery systems is a common example.
- Iron and manganese—Soluble Fe^{+2} and Mn^{+2} ions may be found in well water. These ions are oxidized in the cooling system water. The insoluble oxidized form will behave like other particulate material.

- Corrosion products—These materials can either precipitate in place at the corrosion site or be carried by the water and precipitate in other places in the system.
- Treatment products—Overdosing some treatment chemicals can cause precipitation, generally by a scale formation mechanism.
- Microbial growth—Slime formed by bacteria acts as a binder for other foulants such as silts and scales.

The process of deposition by suspended solids will be briefly described, since this is most widely encountered. Knowledge of the interaction of the particles in suspension is valuable to understand how dispersants can prevent fouling from suspended solids. Fouling by organic contamination such as oils or other process leaks is due to the insolubility of these nonionic compounds in the highly ionic water. Oxidized iron and manganese or corrosion products carried into the system can behave much like suspended particles. Fouling by treatment products is primarily a scale forming mechanism due to precipitation of the treatment with calcium or other positive ions in solution.

Suspended Particle Interactions

The tendency for particles to settle out of solution depends on particle size, surface charge, and the attractive forces between small particles in solution. Larger particles will settle more quickly by gravity. For example, a handful of sand added to a bucket of water will settle rapidly. However, there will be some small particles that settle slowly or will not settle at all. Particles under 1 μm are generally non-settling.

The random motion of particles in solution results in collisions of the particles. This process can be aided by the flow of water in a cooling system. The colliding particles may or may not stick together. This process, called agglomeration, is controlled by the magnitude of the attractive and repulsive forces on the surfaces of particles. The particle surface properties are often more important than the chemical composition of the particle.

Attractive and Repulsive Forces

The size of the particle, its density, and surface charge are key factors in determining whether agglomeration occurs. Electrostatic charges exist on the surface of suspended particles in water. The surface charge develops either by adsorption of charged ions from the solution or by dissociation of surface molecules into the solution. The charge on the particle surface must be compensated by an ion of opposite charge (a counter-ion) nearby in solution. Many of these counter-ions, especially at high surface charge density, are tightly

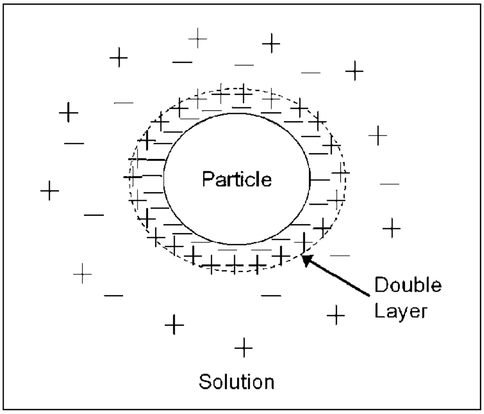


Figure 15.10 A suspended particle in water has a surface charge that is balanced by a layer of nearby ions in solution, which is called the ionic double layer.

held near the surface. The rest of the counter-ions form a more diffuse ionic atmosphere around the particle, as shown schematically in Fig. 15.10. This distribution of charge is generally referred to as the electrical double layer.

The net effect is that each particle with its surrounding double layer is electrically neutral. When two particles approach each other, the ionic atmospheres of the two particles overlap. Energy is required to change the distribution of counter-ions so that this overlap can occur. In a stagnant solution, that energy is generally not available; hence, the particles repel each other, despite overall electroneutrality. In cooling water systems, the flow of water can provide the needed energy to remove the double layer, allowing the particles to come close enough to attract each other. In addition, the presence of divalent and trivalent cations can destabilize the particles and increase agglomeration. This is why materials like alum (containing Al^{+3} ions) and ferrous sulfate (source of Fe^{+2}) are used in clarification of water containing suspended material.

Agglomeration and Growth

As the agglomerated particles grow, larger particles begin to settle, just like a larger, single grain of sand. The more suspended solids in a system, the greater the possibility of fouling deposition. This allows for more collisions between particles, which can result in more agglomeration. Surface characteristics of the system have an effect upon the physical nature of the deposit once particles have settled. Thus, the potential deposition on a relatively rough surface such as mild steel, is greater than for a smooth surface such as copper or stainless steel. An increase in deposition potential also occurs when the depositing material consists in part of sticky particles such as microorganisms.

Suspended Solids Deposition Processes

Once fouling by suspended material begins, deposits may continue to grow indefinitely, or the rate of fouling may slow down. Kern and Seaton proposed a model where the rate of fouling would slow down asymptotically over time. This evolved from their observation that fouling in industrial heat exchangers often slowed to a low rate after sufficient time. Kern and Seaton proposed that the net fouling rate was the difference between a deposition process and a removal process, both of which occur simultaneously. The removal process can also be thought of as release of material back into the flow or re-entrainment. The possibility that both deposition and release exist simultaneously can be explained by turbulent flow phenomenon in water. As conditions fluctuate in a turbulent stream, deposition can occur in areas that are more quiescent. Removal can be due to bursts of turbulence at a surface that shear particles from that surface. Reduced deposition can also be due to increased turbulence, as deposits create a rough surface or as velocity increases through the reduced diameter of tubing. Turbulent flow in exchangers is well known to help minimize fouling.

Cooling Systems Deposits

Deposits in cooling systems can be composed of a number of materials. Following are the more common scales and foulants.

Calcium Carbonate

A common mineral scale in cooling water systems is calcium carbonate ($CaCO_3$). Its solubility decreases as temperature increases (inverse solubility). Solubility also decreases as pH increases. Calcium carbonate forms hard, tenacious scale and can exist as calcite, aragonite, and vaterite. Calcium carbonate formation depends upon the complex balance between calcium, carbon dioxide, bicarbonate, and carbonate in cooling water. Any change that drives the equilibrium reaction toward calcium carbonate (such as increasing the temperature or pH) will tend to cause precipitation. The same phenomena that describe lime softening reactions apply to the precipitation of this scale.

Calcite is the most stable form of calcium carbonate and can exist in a variety of crystal forms. Calcite is the form of calcium carbonate most often found in cooling systems (Fig. 15.11). Aragonite is less common and less stable than calcite. Calcite is the principal constituent of limestone, and aragonite is most commonly found in pearls. Aragonite generally forms at higher temperatures compared

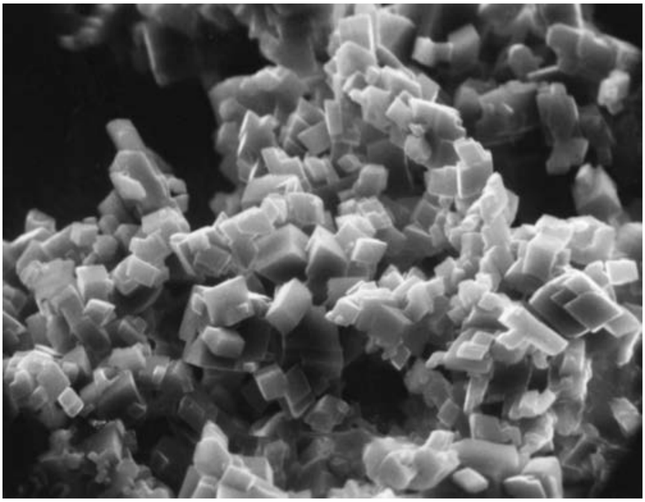


Figure 15.11 Example of calcite crystals, the more common crystalline form of calcium carbonate.

to calcite. Aragonite can have a variety of crystal structures, several of which include needle-like crystals (Fig. 15.12). Impurities in the water such as magnesium, strontium, or barium will sometimes cause preferential formation of aragonite over calcite, or increase the percentage of aragonite in mixed deposits.

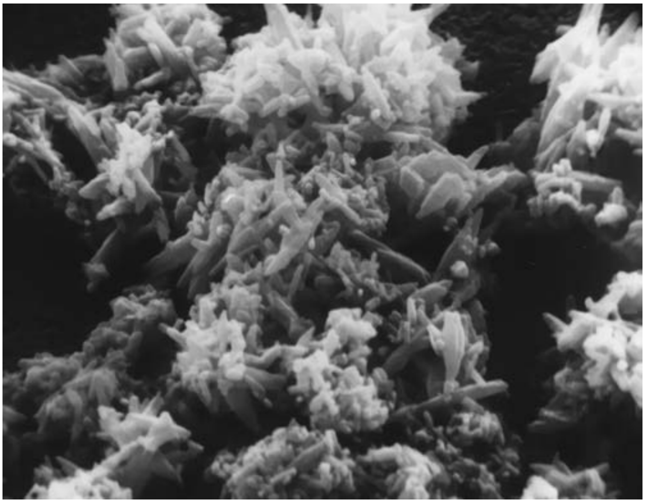


Figure 15.12 Aragonite is a form of calcium carbonate that sometimes appears as needle-shaped crystals.

Under field conditions, calcium carbonate is white or light brown and might be combined with other minerals. If formed rapidly, calcium carbonate can be porous and amorphous in nature. Often, calcium carbonate deposits in cooling systems are a combination of calcite and aragonite.

Calcium Sulfate

Calcium sulfate is relatively soluble compared with other scales like $CaCO_3$, and is not often a problem in cooling water applications. This mineral is found in cooling towers operating at high concentration ratio such as in power generation and in brackish water applications. Sulfuric acid, used for pH control, will increase the sulfate concentration in cooling water. Potential forms of calcium sulfate are anhydrite ($CaSO_4$), hemihydrate ($CaSO_4 \cdot \frac{1}{2} H_2O$), and gypsum ($CaSO_4 \cdot 2H_2O$). Gypsum is the natural mineral form of calcium sulfate. Gypsum is directly soluble with temperature; the anhydrite form is inversely soluble with temperature. Gypsum is stable below 150°F (66°C), and anhydrite above this temperature. This means that gypsum could precipitate in cooler regions of the system like the tower fill, whereas the anhydrite might be found on a hot heat exchanger.

For precipitation to occur, calcium usually must be greater than 800 to 900 mg/L (as $CaCO_3$), and sulfate needs to be very high (>5000 mg/L as Na_2SO_4). This is illustrated in Fig. 15.7 shown earlier. Note in this figure that calcium sulfate is soluble at higher calcium values if the sulfate concentration is less than 5000 mg/L as Na_2SO_4. However, concentration mechanisms that occur under deposits or in small crevices can cause $CaSO_4$ precipitation, even though bulk water concentrations of calcium and sulfate ions may not be at these levels. Calcium sulfate deposits are generally mixtures of various forms, as is the case with $CaCO_3$. In many cases, gypsum is found with the anhydrite or hemihydrate forms.

Silica and Silicates

The terms silica and silicates are often used interchangeably, even though silica and silicate represent two distinct types of compounds. These terms should not be used interchangeably. Silica refers to SiO_2. Silicate refers to compounds, which are formed by reacting ionized silica (SiO_3^{-2}) with metals such as calcium, magnesium, aluminum, iron, zinc, etc. Clays such as kaolinite and illite are examples of silicates found in cooling water as water-borne silt deposits. The variety of forms indicates the complexity of silicon chemistry. Silica deposition is a result of polymerization of silicic acid or biological activity in the water. Silicate deposits are often due to coprecipitation with other minerals, precipitation with multivalent cations, and fouling by silt. Several of these processes may take place concurrently, making prediction of equilibrium solubility difficult.

When silica or silicate is found in either water or a deposit, the analysis results are reported as SiO_2, regardless of whether the compound present is silica or silicate. The use of SiO_2 in expressing elements identified in a deposit sample, whether silica or silicate is present, assumes that an oxygenated form of silicon (Si) is present. Proper interpretation of water and deposit analyses along with an understanding of the variables contributing to silica or silicate deposition, is critical for assessing and correcting operating conditions, which result in deposition.

Common rules of thumb have been used to indicate whether silica-based scale can occur. These rules may indicate a general tendency for scale to form but cannot consider the complexity of a cooling water system. Therefore, rules of thumb should be used with caution. Computer models for solubility prediction should be used, because simple indices or graphs cannot consider all the aspects of silica and silicate scaling accurately.

Silica Deposits

Silica scale (SiO_2) is extremely tenacious, highly insulating, and very difficult to remove. Silica deposits are usually found as amorphous silicon dioxide. Silica scale is unusual and may occur only when the level of SiO_2 in the recirculating water exceeds 150 mg/L and temperature is below 70°F (21°C). Silica forms an equilibrium in water between silicic acid (H_2SiO_3) and silicate ions (SiO_3^{-2}). The solubility of silica increases as the pH increases (more silicate ions), as shown in Fig. 15.13. However, pH usually cannot be increased enough to prevent silica deposition, because other minerals then become

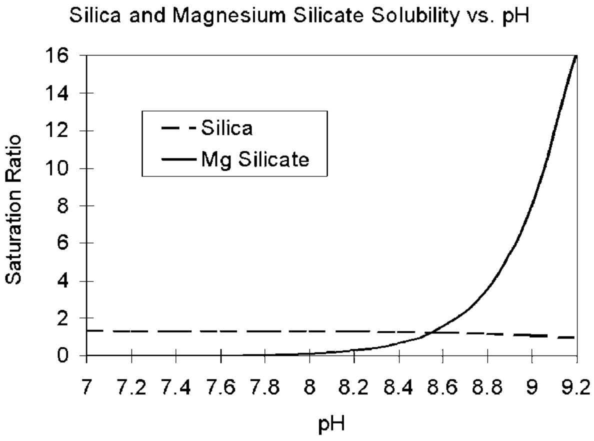


Figure 15.13 Silica solubility at 95°F (35°C) increases (lower saturation ratio) very slightly as pH increases, but magnesium silicate solubility decreases rapidly above pH 8.5.

less soluble. For example, magnesium silicate ($MgSiO_3$) becomes a more serious scaling problem as the pH increases above 8.5; therefore, care must be taken not to trade SiO_2 scale for $MgSiO_3$ scale. The system should be monitored for scale very closely when running a high pH and high-silica concentration, because the formation of any scale will encourage the coprecipitation of silica and magnesium silicate.

Silica solubility increases with temperature. In high-silica waters, precipitation generally occurs in the cooler sections of a cooling water system. The maximum concentration of silica that can be tolerated in a recirculating cooling tower depends on several factors, such as inhibition of other minerals, corrosion control, biological control, and in general, the cleanliness of the system.

Living organisms such as diatoms can also be represented in deposit analyses as silica. These organisms remove silica from dilute solution to create their skeleton in precisely controlled structures of intricate design, almost perfect to molecular dimensions (Figs. 15.14 to 15.16).

Magnesium and Aluminum Silicates

$MgSiO_3$ is a very tenacious, glassy-type scale that is difficult to remove except by mechanical or extreme chemical cleaning methods. Magnesium silicate precipitation is influenced greatly by pH, Mg, and SiO_2 levels. Generally, the pH must be greater than 8, depending on SiO_2 level, before $MgSiO_3$ precipitates. $MgSiO_3$ precipitation exhibits inverse solubility with increasing temperature. Consequently, scale will be more severe on heat transfer surfaces, especially when low-flow conditions exist.

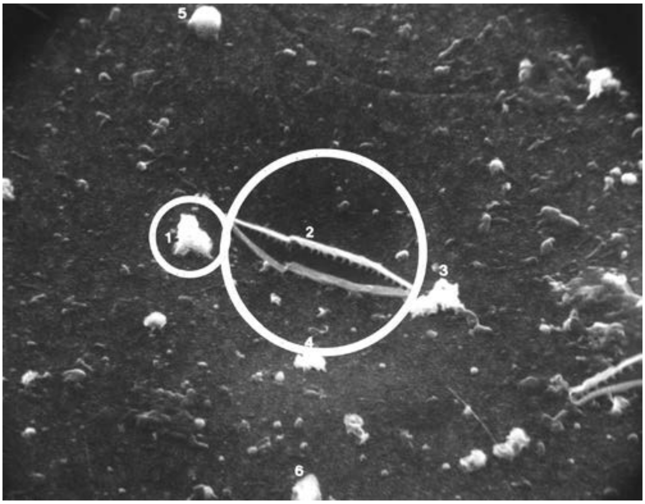


Figure 15.14 Scanning electron micrograph of particulates in a water sample.

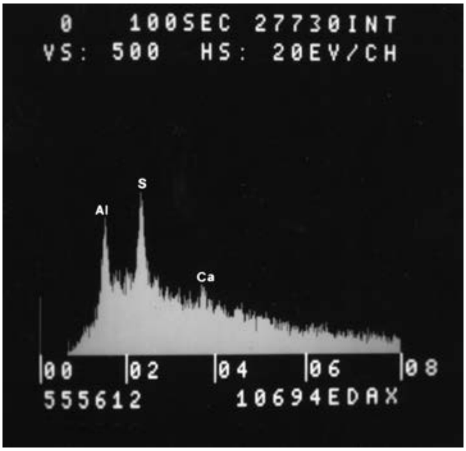


Figure 15.15 X-ray diffraction analysis of particles 1 and 3 identified as a precipitate containing calcium, sulfur, and aluminum.

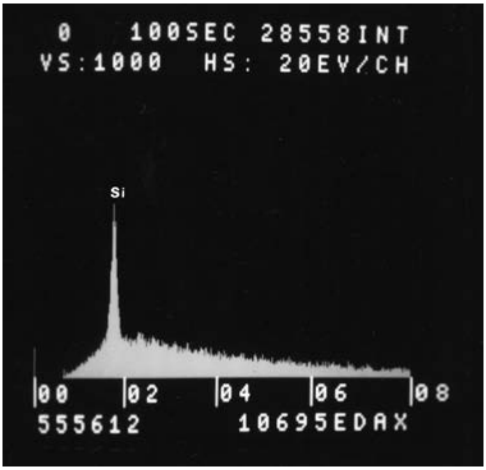


Figure 15.16 X-ray diffraction analysis of particle 2 identified as a diatom, which is mostly silica.

Other factors that affect $MgSiO_3$ precipitation include high heat flux, bulk water temperature, and the Ca/Mg ratio. When the magnesium level is equal to or greater than the calcium level, the potential for $MgSiO_3$ scale greatly increases. $MgSiO_3$ precipitation normally accompanies precipitation of $CaCO_3$ in water containing appreciable silicate.

The presence of aluminum ions in water will reduce silica solubility. However, aluminum silicate deposits are most commonly due to deposition of silt.

Calcium Phosphate

Calcium phosphate, like calcium carbonate, exhibits an inverse solubility with increasing temperature and becomes less soluble as pH increases. The combination of calcium, orthophosphate, temperature, and high pH is extremely conducive to the deposition of calcium phosphate.

Calcium phosphate is much less soluble than calcium carbonate. As little as 1 to 2 mg/L orthophosphate (as PO_4) can result in extreme calcium phosphate scaling, when the calcium concentration is 200 to 1000 mg/L (as $CaCO_3$). Even in soft water localities, slightly higher orthophosphate concentrations can still create calcium phosphate scale. Figure 15.17 shows the solubility of calcium phosphate under a variety of cooling water conditions.

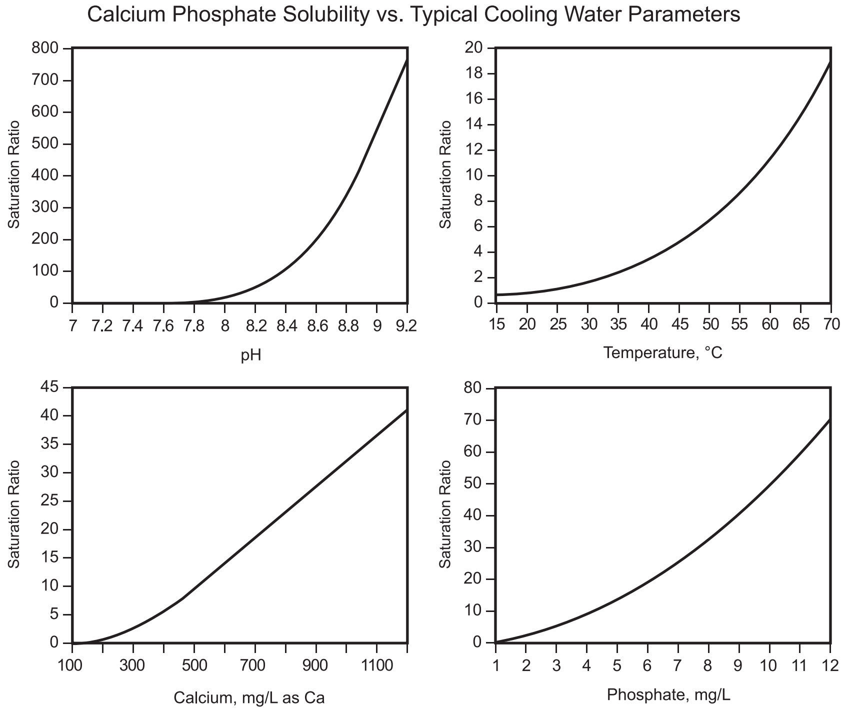


FIGURE 15.17 Calcium phosphate solubility as a function of pH, temperature, calcium concentration, and phosphate concentration. Calcium is 625 mg/L as $CaCO_3$, orthophosphate is 2 mg/L as PO_4, and pH is 7.5 (except in graphs where calcium, phosphate, or pH vary). Other components are typical of cooling tower conditions.

Orthophosphate can come from a number of sources. In some regions of the world, the makeup water used for a cooling system can contain naturally occurring orthophosphate. In other places, the makeup water may contain phosphates that have been added as a corrosion inhibitor for the water distribution piping. These inhibitors could be either orthophosphate or polyphosphates, which are condensed phosphates that can break down to orthophosphate in water. This breakdown or reversion process is often aggravated by increasing temperature and pH that occurs in cooling systems. Polyphosphates are also used in some cooling system treatments, both as a corrosion inhibitor directly and as a source of orthophosphate through reversion. A third source of orthophosphate is the phosphonates that are often used for scale control. Several of these phosphonates are sensitive to degradation by oxidizing biocides used for microbial control. One of the degradation products is orthophosphate. Therefore, this is another example of the need for good control of cooling system operating parameters to minimize the potential for deposition from the various sources of orthophosphate.

A variety of calcium phosphate forms can exist, such as amorphous calcium phosphate, tricalcium phosphate, or hydroxyapatite (HAP). The initial stages of precipitation often produce amorphous calcium phosphate, which transforms over time into HAP. As a result, deposits containing calcium phosphate often contain mixed phases of calcium phosphate.

Aluminum ions can significantly affect the solubility of phosphate in cooling water. Aluminum phosphate is a highly insoluble white scale that forms whenever aluminum ions and phosphate are present in the water. This deposit is primarily a result of aluminum carryover from a clarifier. The aluminum ions can cause insoluble aluminum phosphate floc to form in the bulk solution, which then acts as a foulant. Soluble aluminum ions should be eliminated from the makeup water, when phosphate is present in the cooling water.

Zinc Deposits

Dissolved zinc ions are effective at corrosion inhibition, particularly for steel and cast iron. However, zinc ions can precipitate and contribute to scaling. Zinc-based scales are generally soft and loose. Zinc hydroxide, carbonate, and phosphate all occur, depending on the water chemistry and inhibitor programs in use. Each of these zinc precipitates is normally less soluble at higher pH (>7.5), and each precipitate has different solubility as a function of increasing temperature. Zinc hydroxide is less soluble at higher temperatures, zinc phosphate is more soluble at high temperature, and zinc carbonate is only slightly less soluble as temperature increases (Fig. 15.18). The solubility of zinc phosphate is one of the reasons why the combination of orthophosphate and zinc is a good corrosion control program at alkaline pH.

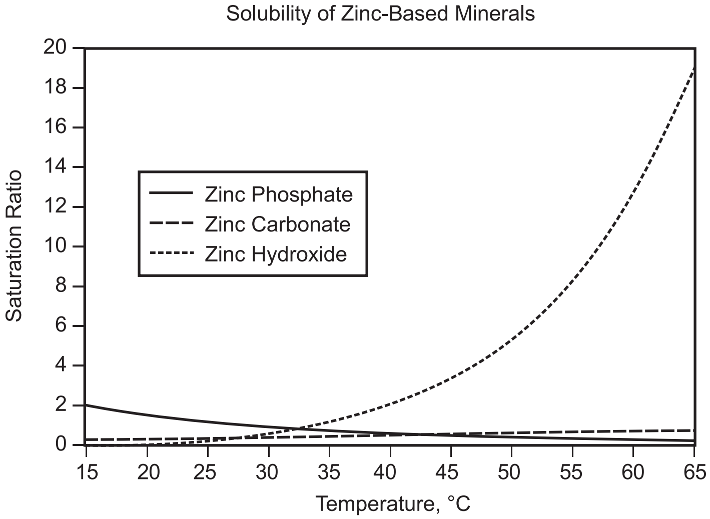


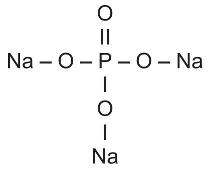
Figure 15.18 Solubility of zinc species as a function of temperature.

Zinc deposits can result from an overfeed of a zinc-based treatment program. Zinc carbonate ($ZnCO_3$) can also result from corrosion of galvanized metal. This "white rust" is usually found on the galvanized metal surface where the corrosion occurs, rather than in other parts of the system. White rust is covered in more detail in Chap. 16 on Cooling System Corrosion.

Zinc deposits are often non-tenacious but cause problems in low-flow heat transfer areas. However, zinc deposits can form on heat exchangers with higher flow, when overfeed conditions exist. When bulk precipitation occurs, the zinc-based scale that forms is not protective as a corrosion inhibiting film. As with all scale, this can lead to under-deposit corrosion. Use of specialized dispersants at higher pH (>7.8) will inhibit zinc deposition. The dispersants that are normally effective on calcium phosphate will generally prevent zinc hydroxide and zinc phosphate scale too.

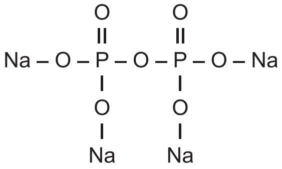
Calcium Polyphosphates

Polyphosphates have been used in water treatment for many years, but are used less frequently now because of reversion and environmental issues. Polyphosphates are commonly used in municipal water systems to prevent corrosion and minimize "red water" problems caused by soluble iron (ferrous ions) in the water. Polyphosphates are simply polymers of orthophosphate. A variety of forms exists from a simple combination of two phosphate molecules (pyrophosphate) to long-chain "glassy" phosphate molecules. Examples of phosphate molecules are shown in Fig. 15.19.



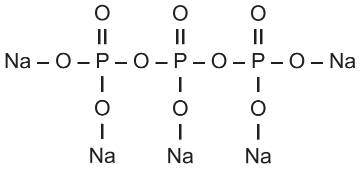
$\mathrm{Na{-}O{-}P({=}O)(O{-}Na){-}O{-}Na}$

Sodium Orthophosphate



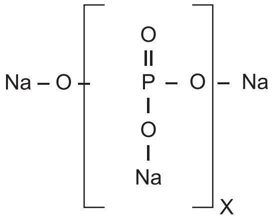
$\mathrm{Na{-}O{-}P({=}O)(O{-}Na){-}O{-}P({=}O)(O{-}Na){-}O{-}Na}$

Sodium Pyrophosphate



$\mathrm{Na{-}O{-}P({=}O)(O{-}Na){-}O{-}P({=}O)(O{-}Na){-}O{-}P({=}O)(O{-}Na){-}O{-}Na}$

Sodium Tripolyphosphate



$\mathrm{Na{-}O{-}[P({=}O)(O{-}Na){-}O]_{X}{-}Na}$

Where X ⩾ 4

Long-Chain Glassy Phosphate

Figure 15.19 Various polyphosphate structures.

Polyphosphates create two problems in cooling water systems. First, calcium polyphosphates have limited solubility in typical cooling water conditions. Polyphosphates form a weak complex with calcium in water. The solubility will vary depending on the type and concentration of polyphosphate, calcium, temperature, pH, and other factors. Figure 15.20 shows the solubility of calcium pyrophosphate to illustrate some of the factors that affect its solubility.

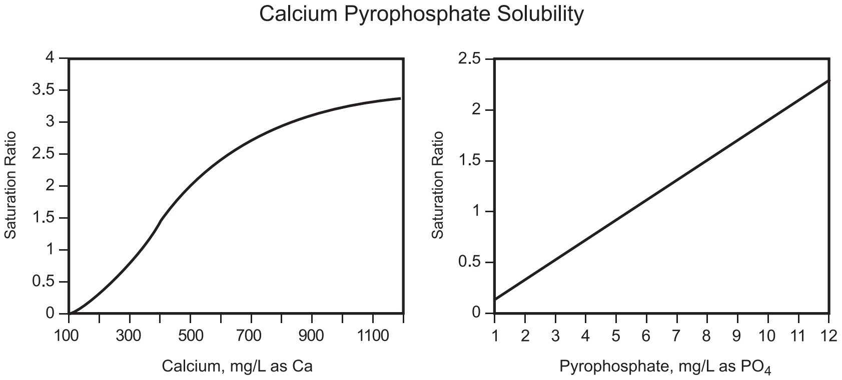


FIGURE 15.20 Calcium pyrophosphate solubility as a function of calcium and pyrophosphate concentrations. Pyrophosphate is 5 mg/L as PO_4 on the left, and calcium is 750 mg/L as $CaCO_3$ on the right. Temperature is 95°F (35°C), and pH is 7.5 in both charts.

Second, polyphosphate will break down to orthophosphate when dissolved in water. This is called reversion, and the resulting orthophosphate can cause deposition problems through precipitation of calcium orthophosphate. There are many factors that affect this reversion process, including the pH of the water, temperature, time, presence of trivalent ions, and microbial organisms in the water.

Calcium Phosphonates

Phosphonates are organic phosphate compounds, where the phosphorous is bonded directly to a carbon atom (C–P bond) on the organic molecule. There are various organic phosphate compounds available, which are effective scale control agents for calcium carbonate or calcium sulfate, for example. Phosphonates are much less prone to reversion to orthophosphate than are the polyphosphates. Examples include:

- AMP—aminotris-methylenephosphonic acid
- HEDP—1-hydroxyethylidene-1,1-diphosphonic acid
- PBTC—phosphonobutane-1,2,4-tricarboxylic acid
- PAPEMP—Polyamino polyether methylene phosphonate

Calcium salts of some phosphonates are insoluble and can contribute to scaling when misapplied. When applied at proper dosages, calcium phosphonate precipitation is minimal. The greatest problems occur if the phosphonates are overdosed or the calcium concentration is too high. As the calcium increases above 1200 mg/L, or the dosage of some phosphonates increases above 5 to 10 mg/L, precipitation can occur. Of the most common phosphonates, HEDP and AMP are the most sensitive to calcium precipitation. PBTC is the next most sensitive. PAPEMP is very soluble in the presence of calcium and is a very effective calcium carbonate inhibitor.

Iron

Iron oxides are often considered either a foulant or a scale. The cause of iron precipitation is different depending on the source of the iron, but the problem is equally serious. One of the most common forms of iron deposits is the oxide in corrosion products (rust). Iron is usually present to some degree in all cooling water deposits. Most often, an iron deposit looks like rust, but when combined with other minerals, iron deposits could appear as general foulants like silt.

Iron in Makeup Water

Subsurface waters (wells) may contain soluble iron in the ferrous form (Fe^{+2}). When water containing ferrous ions is aerated or chlorinated, the soluble ferrous ion is converted to the insoluble ferric form (Fe^{+3}). The result is a colloidal form of ferric hydroxide or ferric oxide [$Fe(OH)_3$ or Fe_2O_3], which exhibits a red color (red water). Iron oxides vary considerably in both physical and chemical characteristics: some are hard, dense, highly adherent deposits; others are loose, highly porous deposits. Some are reddish Fe_2O_3 deposits; others are black, highly magnetic iron oxide (Fe_3O_4) deposits. At normal pH values, iron oxide is not soluble in cooling water systems.

Corrosion Products

The corrosion of iron-based metals like mild steel or cast iron will release Fe^{+2}. If conditions are right, this can quickly oxidize to an insoluble, passive iron oxide film, which reduces corrosion. If the Fe^{+2} ions diffuse away from the metal surface before being oxidized, deposition will occur as fouling in other areas. Under non-passivating conditions, the initial Fe^{+2} can be oxidized to Fe_2O_3, and voluminous corrosion products can form at the site of corrosion. Figure 15.21 shows an example of iron corrosion products on a steel pipe.

Influence of Bacteria

The precipitation of iron may be aggravated by the presence of iron-depositing bacteria. These bacteria are common in natural waters but less common in oxygenated cooling systems. The two most common species are *Gallionella* and *Sphaerotilus*. Both species oxidize soluble ferrous ions to insoluble ferric ions to create energy for growth. Under-deposit corrosion can often result from these deposits.

Iron Phosphates

Ferric phosphate ($FePO_4$) is seldom seen as a pure scale of just iron and phosphate, but often as a mixture with other minerals or suspended solids. This mineral is normally found in phosphate-treated

Figure 15.21 Corrosion products containing iron oxides on a steel pipe can create voluminous deposits, almost plugging this utility service water pipe.

systems, when iron is present at high levels in the makeup water. Typically, iron oxide or hydroxide will coprecipitate with calcium phosphate to form a yellowish-white precipitate.

Silt

The term silt refers to a combination of suspended, insoluble particles that can contaminate a cooling system. Silt commonly consists of silica and alumina compounds from the earth's crust. River water silt particle size is 1 to 100 µm. Silt can generally enter a system in two ways:

1. Makeup water—Well waters are generally low in silt and suspended solids and of consistent quality. Surface waters (rivers or lakes) generally have higher amounts of silt, and the quality of water is greatly influenced by environmental factors such as runoff after a heavy rain or upsets in a lake. The quantity of silt in surface waters can vary considerably from day to day. Makeup waters with varying suspended solids are shown in Table 15.2.
2. Airborne contamination—The geographic location and local environment affect the type and amount of wind-blown dust entering a system. Cooling systems located in flat, open, windy areas accumulate silt faster than cooling systems in sheltered areas.

Constituent (mg/L Except Conductivity)	Well	Well	Lake Hudson	Lake Superior	Willow River	Mississippi River
Aluminum (Al)	<0.1	<0.1	0.3	<0.1	0.2	0.4
Calcium ($CaCO_3$)	230	160	110	34	55	110
Magnesium ($CaCO_3$)	52	83	26	11	21	84
Silica (SiO_2)	9.7	9.6	5.9	2.5	10	9.0
Sodium (Na)	4.4	75	22	1.7	2.5	13
Chloride (Cl)	5.3	43	14	2.8	1.6	19
Sulfate (SO_4)	48	86	26	4.0	6.0	36
M alkalinity ($CaCO_3$)	240	220	120	45	62	150
P alkalinity ($CaCO_3$)	<10	<10	<10	<10	<1	<10
Conductivity (µS/cm)	560	790	320	100	150	410
Suspended solids (Total @ 105°C)	<1.6	<1.6	9.9	<1.5	9.3	25

Table 15.2 Differences in Makeup Waters from Wells, Rivers, and Lakes

Mud and silt from turbid waters usually form hard, baked-on deposits on heat transfer surfaces. Mud and silt have a tendency to settle in low-flow (low-velocity) areas of a system, causing deposits. Additionally, mud and silt can be easily incorporated into other deposits, thus increasing the volume and insulating characteristics of the deposit. A deposit that is made up of mostly silica and aluminum is likely a silt deposit. The typical ratio of silica to aluminum is 3:1 as SiO_2 to Al_2O_3. There may also be small amounts of potassium or titanium in a silt-based deposit (Table 15.3).

Manganese

The solubility properties of manganese are similar to iron. Like soluble iron, manganese is found in some groundwater sources. Unlike iron, some soluble manganese can be found in some river water sources. Manganese is not readily oxidized by dissolved oxygen, but will be oxidized by chlorine and hypochlorite causing a precipitate in cooling systems.

Constituent	Form Reported	Percent in Dried Sample
Silica	SiO_2	52
Alumina	Al_2O_3	18
Iron*	Fe_2O_3	11
Calcium	$CaCO_3$	14
Potassium	K_2O	3
Titanium	TiO_2	2

*Iron may be from corrosion products.

Table 15.3 Analysis of Deposit Caused by Silt

Several factors are peculiar to manganese fouling:

- The oxidation of manganese occurs at a moderate rate. As a result, some manganese may reach heat transfer surfaces in the soluble form, and then rapidly be oxidized, becoming adherent and very difficult to remove. On the other hand, some manganese oxidation occurs in the bulk water, forming a foulant, which then deposits on the heat transfer surface.
- The oxidation of manganese is autocatalytic in nature; that is, the oxidation reaction is catalyzed by the presence of manganese dioxide compounds. This means that deposits may be slow to appear, but eventual oxidation of a small portion of the available manganese can catalyze heavy deposition.
- Manganese dioxide is extremely tenacious and difficult to remove by mechanical means normally used to clean heat exchangers and condensers.
- Manganese dioxide can cause under-deposit corrosion, particularly on copper alloys and stainless steel.

These factors make manganese a special problem unlike deposits caused by oxides of other metals. For example, deposits from corrosion of iron are objectionable, but generally not as tenacious or hard. Additionally, iron deposition is not autocatalytic, so the rate of iron oxide deposition does not escalate after the first deposits form.

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CHAPTER 16

Cooling System Corrosion

Heat exchange equipment and piping in cooling water systems is made of various metals that are subject to the same problems that affect automobiles, tools, household plumbing, bridges and other metal products. If not properly treated, these metals seem to self-destruct when exposed to water in cooling water systems. This natural series of changes is called corrosion. Corrosion returns processed metals such as steel, copper, and zinc to their native oxide states as chemical compounds. This process of corrosion must be understood if long-term reliability of cooling water system operation is to be achieved.

Iron in its natural state is an oxide (e.g., Fe_3O_4, FeO, and Fe_2O_3). When processed into iron and steel, the oxygen is driven off to form pure iron (Fe°). Energy is required to transform the oxide into the metal. In the presence of water and oxygen, nature relentlessly attacks steel, returning the elemental iron (Fe°) back to an oxide, usually some combination of hematite (Fe_2O_3) and magnetite (Fe_3O_4).

In cooling water systems, corrosion is a serious problem. Cooling equipment designed for years of service may fail within months. If corrosion is not kept under control, heat exchangers will become inefficient because of corrosion deposit buildup, and equipment will be ruined because of leaks. All of these problems cost money in terms of increased maintenance, equipment repair or replacement, and lost production.

The annual global cost of corrosion is estimated to be \$2.2 trillion according to The World Corrosion Organization.[1] Costs included the effect of corrosion of all types of equipment, not just cooling water systems. The costs included corrosion control methods, services, and the economic impact for specific industry segments, such as transportation, infrastructure, and industry. The estimated costs were \$6.9 billion/year for the electric utility industry and \$17.6 billion/year

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[1] The World Corrosion Organization, 2016, http://corrosion.org/

for production and manufacturing. This study did not include indirect costs for lost production or lost reliability, so the true cost of corrosion is even higher.

Based on the information in this study, the global costs of cooling water corrosion, including lost efficiency and lost production, are in the billions of dollars per year. Fortunately, corrosion can be controlled with proper treatment and automated monitoring and control. This chapter will focus on what corrosion is, how corrosion occurs, and the problems corrosion causes.

Corrosion of Materials in Cooling Systems

Cooling water systems can be fabricated using a number of different metals and materials, each with unique corrosion issues. Some of the more common materials and corrosion mechanisms will be discussed here. For more detailed information, refer to *The Nalco Guide to Cooling Water Systems Failure Analysis*, 2nd ed.[2]

Carbon Steel

Mild or carbon steel is one of the most economical materials for construction of heat exchangers and cooling water systems. However, this metal is easily corroded in oxygenated cooling water. Carbon steel undergoes a wide variety of corrosion mechanisms, all impacted by the corrosivity of the water due to dissolved ions and dissolved oxygen. Carbon steel is sensitive to pH and suffers significant corrosion at low pH (acid conditions). The corrosion rate drops as the pH increases over 8.5, but corrosion increases at very high pH (caustic conditions over pH 12). As with other chemical reactions, corrosion increases with temperature. Consequently, high-heat-flux or high-temperature exchangers will suffer greater metal loss than transfer piping.

Corrosion products are generally brown or orange iron oxides. The corrosion products can form a protective oxide film on the metal surface that limits further corrosion, or the metal oxides can become a porous deposit that is not protective. Iron oxide deposits can also result from soluble iron in the water, which forms nonprotective deposits. Cooling systems that operate with carbon steel heat exchangers are particularly challenging. In these systems a very effective steel inhibitor along with good system control will pay dividends of improved operation and longer exchanger working life. A dense, passive film can form on the steel surface with the right inhibitor and concentration. Properly controlled cooling water programs can maintain corrosion at acceptable rates [generally considered

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[2] Dillon, J., Desch, P., Lai, T., *The Nalco Guide to Cooling Water Systems Failure Analysis*, 2nd ed, Ed Flynn, D., McGraw-Hill, 2015.

<3 mpy (76 µm/y)]. Cooling systems that operate with carbon steel heat exchangers are particularly challenging and will benefit by using a very effective steel inhibitor along with good system control.

Copper Alloys

Copper and copper alloys are probably the next most commonly encountered metals in cooling water systems. These alloys are used when the metal is compatible with the process fluid to be cooled and the high thermal conductivity of copper is needed. Copper may be found in heating or cooling coils in building heating and chiller systems, domestic water systems, and in the molds of continuous caster systems in steel mills. In cooling tower systems, heat exchangers can often be made of admiralty brass, which contains copper, zinc, tin, and antimony or arsenic as alloying agents. In large power utility condensers, cupro-nickel alloys may be used to further minimize the damage from corrosion and erosion.

Copper alloys are more resistant to corrosion by oxygenated water than carbon steel. Copper alloys are on the borderline between immunity from corrosion and active corrosion. Oxidizing agents like halogens can push copper alloys into the corrosive state. The production of corrosion products is much less significant for copper alloys than for carbon steel, because copper alloys are more corrosion resistant. The cupric ions (Cu^{+2}) that form as an oxidation product of copper corrosion are much more soluble than the ferric ions (Fe^{+3}) from iron corrosion. Copper ions from makeup water or corrosion byproducts can attach to less noble metal such as steel or aluminum surfaces setting up conditions for galvanic corrosion. Corrosion of copper and its alloys can be influenced by dissolved carbon dioxide, chloride, and ammonia. Chlorination of cooling water can increase corrosion of copper and its alloys. Precipitation of manganese dioxide can induce localized corrosion in copper alloys. Deposition of other materials on the surface can promote under-deposit corrosion. If the surfaces are kept clean, general corrosion rates of less than 0.2 mpy (5 µm/y) are considered acceptable. This is possible with effective treatment programs and system control.

Stainless Steel

Steel can be made “stainless” or highly corrosion resistant by inclusion of 11% or more chromium to form an alloy. There are many grades of stainless steel available. The most common are the austenitic stainless steels (304 and 316). The 304 grade contains 18 to 20% chromium and 8 to 10% nickel, hence 304 stainless steel is often called 18/8 stainless steel. The 316 grade adds 2 to 3% molybdenum in addition to chromium and nickel.

Stainless steel is very corrosion resistant in clean cooling water systems. In the presence of dissolved oxygen, a dense, highly adherent film of chromium oxide is formed on the surface, which prevents further corrosion. Stainless steel is an example of a self-passivating metal. Corrosion problems can occur in dirty systems, however. Stainless steel is susceptible to under-deposit corrosion, crevice corrosion, and stress corrosion cracking (SCC), particularly as the chloride content of the cooling water increases. SCC affects the austenitic stainless steels in waters that contain chloride. Other forms of stainless steel are more resistant to chloride stress corrosion cracking. However, the type 304 and 316 austenitic forms are the most commonly used. Surface cleanliness is important to minimize the tendency for under-deposit corrosion, crevice corrosion, and SCC.

Galvanized Steel

Galvanized steel generally involves a coating of zinc metal on the surface of carbon steel. This coating may be produced by dipping the steel in molten zinc or by electroplating. Galvanized metal is used in cooling water systems in panels or in piping. Galvanized metal is most commonly used in small to medium sized prefabricated cooling towers and evaporative condensers. The zinc layer is both a protective coating and a sacrificial anode. The zinc is much less noble than the underlying carbon steel. Therefore, the zinc will corrode sacrificially to protect the underlying steel. After the zinc corrodes through, and large surface areas are exposed, the steel will corrode at the same rate as ungalvanized carbon steel. At temperatures above 140°F (60°C), the polarity of the iron/zinc galvanic couple reverses, resulting in excessive corrosion of the iron. Galvanized steel should not be used above that temperature.

Some corrosion of galvanized coatings on steel is normal. When galvanized steel is exposed to a neutral pH, moderately hard water environment, a surface barrier of nonporous zinc carbonate and zinc hydroxide forms to prevent further rapid corrosion of the zinc coating. However, corrosion becomes excessive under certain conditions such as high pH or low hardness. Galvanized steel that has been attacked by excessive corrosion will have two different appearances. If corrosion is severe, all the galvanized coating will be removed, exposing the unprotected steel. In these cases, the steel can rust, giving the normal, rusty-brown or black appearance of corroding steel. In less severe cases, the zinc coating can be corroded to form what is known as “white rust” (Fig. 16.1). White rust is an unprotective form of zinc hydroxide or zinc carbonate on the surface of the metal. White rust corrosion is often identified because the deposit has a porous, soft, gelatinous, or waxy appearance. White rust can be very similar to a protective zinc oxide coating that forms on dull gray passivated galvanized metal. Both the protective oxide film and white rust are forms of zinc carbonate and zinc hydroxide. The key difference between white rust and the protective oxide film is that white rust is generally a more voluminous and porous deposit.

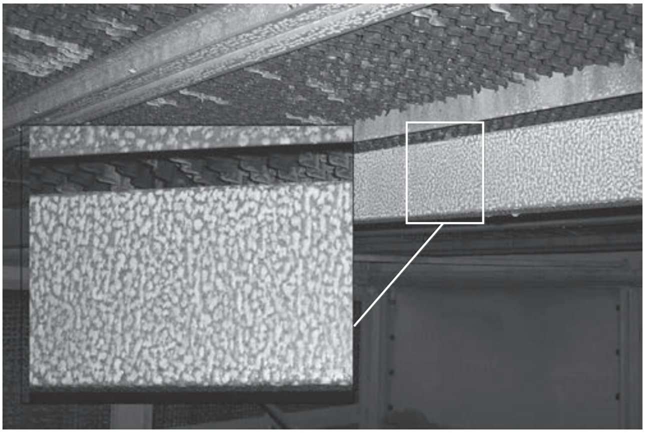


Figure 16.1 Example of white rust on a galvanized steel support beam under the fill section of a cooling tower.

White rust may appear suddenly and progress rapidly over the wetted galvanized areas of cooling towers. A surface covered by white rust is not resistant to further reaction with the aqueous environment, and rapid corrosion may continue. The term "wetted" refers to areas of cooling tower structures that are continually or occasionally wetted. The presence of white rust suggests operation out of the desired control window of pH and alkalinity, or improper passivation of a new or newly cleaned system. White rust corrosion can seriously damage the galvanized zinc coating and shorten the life of the cooling tower. Once the zinc layer has been consumed, corrosion of the mild steel may progress rapidly.

Evaporative condensers often use galvanized coils and tower components to reduce corrosion of the units themselves. Therefore, evaporative condensers often experience white rust.

Nonmetallic Materials

Various nonmetallic materials are used in cooling water systems, ranging from plastic or wood tower fill to concrete in the cooling tower basin. Depending on the environment, degradation of nonmetallic materials can be severe. While not strictly electrochemical corrosion reactions, chemical or biological degradation of nonmetallic materials can be a problem. In some cases, degradation may be worsened by improper treatment or poor control of the cooling tower operating parameters.

Wood in tower fill or support beams can be attacked both chemically and by microbial organisms. (Biological degradation is covered in Chap. 17 on Cooling Water Biology.) Chemical attack can result in delignification. Lignin is the binding material between the cellulose fibers in wood, and loss of lignin weakens the resulting wood structure. Studies have shown that delignification is caused, more by excessively high chlorine levels, than the pH of the water. Proper control of chlorination in alkaline pH treatment programs can significantly minimize the possibility of delignification.

Degradation of concrete can occur at high sulfate concentrations. Most cooling tower basins are now made with sulfate resistant concrete. Acidic pH excursions or poor acid mixing may damage concrete in basins or concrete that may be used to line piping. When feeding acid for pH control, it's a good practice to use an acid-resistant dilution trough to prevent localized acid attack at the acid feed point.

Plastic components and rubber gaskets can be degraded by oxidizing biocides. Most composite materials now used are resistant to chlorine, but with high oxidant concentrations, problems can occur. Materials at and immediately downstream of the oxidizer injection point are most subject to oxidizer attack so attention to the oxidizer feed point and mixing are important to prevent localized feed point oxidizer attack. Common gasket materials may be rendered hard and inflexible, causing the seal to be lost. Plastic tower fill can be degraded by ultraviolet (UV) light, but degradation is minimized by both UV absorbing additives (sunscreen for the plastic) and the location of fill inside the towers.

Therefore, while degradation of nonmetallic components is not often considered a corrosion problem, good system control is necessary to maintain all parts of the system in the best condition.

The Corrosion Process in Cooling Systems

National Association of Corrosion Engineers (NACE), considered to be one of the world's leading authorities on industrial corrosion, defines corrosion as "the deterioration of a material, usually a metal, that results from a reaction with its environment". Corrosion can take many forms; some are oxidation/reduction reactions, while others are physical reactions to the environment or operating conditions. An understanding of corrosion mechanisms helps to identify appropriate corrosion control techniques.

The Local Cell Model

Corrosion is a complex process that can be understood with a simple electrochemical cell, shown for iron in Fig. 16.2. The corrosion cell process can be divided into four steps:

1. Metal loss occurs because of metal oxidation at the anodic area (anode).
2. The formation of metal ions from the metal releases two electrons that flow through the metal.

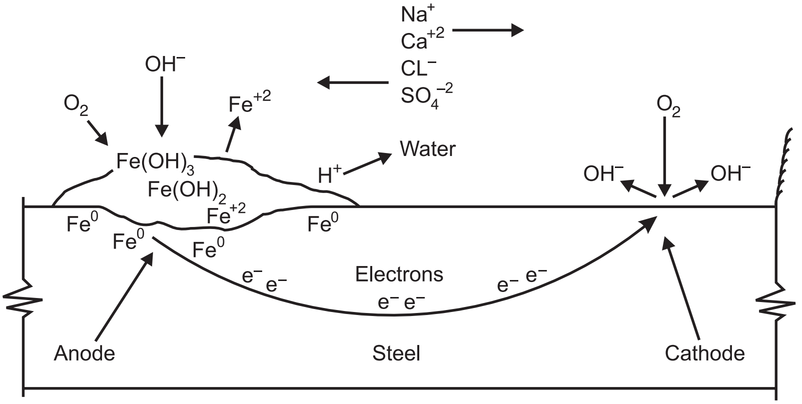


FIGURE 16.2 Metal dissolves at the anode and oxygen is reduced at the cathode in a typical corrosion cell on steel.

3. The electrons react with an oxidant at the cathodic area (cathode).
4. Ions or molecules in solution diffuse to each part of the corrosion cell.

The electron must be thought of as one of the reactants in this process. The anode gains a more positive potential by losing electrons. The cathode moves to a more negative potential because the cathodic area is gaining electrons. The potential difference created in the metal by differences at anodic and cathodic areas is the driving force for the corrosion process. The potential is like the pressure in a water line; the higher the pressure, the higher the flow can be when the line is open. The rate of corrosion is proportional to the current flow (flow of electrons) that results from the potential difference between the anode and cathode. Higher potential can support a higher flow, and thus, a higher corrosion rate.

Diffusion of ions and oxygen through the water occurs for two reasons. Ions diffuse to the surfaces to balance the charges that build up on the metal, because the electroneutrality of the system must be maintained. Cations diffuse toward the cathode to balance the excess of electrons that create a negative charge in these areas. Oxygen diffuses toward the cathode to accept electrons from the metal. The oxygen is reduced by the electrons and forms hydroxide ions, under cooling water conditions. Anions diffuse toward the anode to balance the positive charge created by the metal ions (like Fe^{+2} for iron) that are released into solution by the corrosion process.

While the local cell model is a convenient picture of the process, the anodes and cathodes typically do not stay in one place on the metal surface. Every metal surface is covered with innumerable microscopic-sized anodic and cathodic areas. These sites usually develop from surface irregularities from forming, extruding, and other metalworking operations. Differences in composition of the surface caused by different microstructures in the metal can create an electrical potential difference on the metal surface. Dissolution of metal and reduction of oxygen can occur at any site on the metal surface. An exception to this is that the anode will be stationary during pitting corrosion, or corrosion at a metallurgical feature, such as a crevice or defective weld.

The local cell model is useful to give a mechanistic framework for corrosion processes. This model illustrates the four component processes of corrosion. If one part of the process is stopped, the entire process can stop. Therefore, corrosion control can be based on stopping any of the four components: the anodic reaction, the cathodic reaction, the flow of electrons through surface films, or diffusion of ions to the metal surface.

Anodic Reactions

The reactions at each site of the electrochemical cell are called half-cell reactions, because together, the two reactions form a complete cell. The anodic reaction is the oxidation of the metal to metal ions. The anodic half-cell reactions for iron-based metals and for copper are shown in Eqs. (16.1) and (16.2):

$$\mathrm{Fe^0 \rightarrow Fe^{+2} + 2e^-} \tag{16.1}$$

$$\mathrm{Cu^0 \rightarrow Cu^{+1} + e^-} \tag{16.2}$$

The relative tendency for the anodic reaction to occur is referred to as nobility. Noble metals (gold and platinum) have a lower tendency toward corrosion and require higher potentials for corrosion to occur.

Cathodic Reactions

Cathodic reactions involve the removal of electrons from the metal by the reduction of oxidizing agents. Dissolved oxygen (O_2) in the water moves to the cathodic area and completes the electric circuit by accepting the electrons that are flowing to the cathode. As a result, hydroxide ions (OH^-) are formed at the surface of the metal. Equation (16.3) shows the common cathodic reaction in cooling systems:

$$\frac{1}{2}\mathrm{O_2 + H_2O + 2e^- \rightarrow 2OH^-} \tag{16.3}$$

At low pH (<5), the hydrogen ion (H^+) can take the place of oxygen and complete the electrical circuit, as shown in Eq. (16.4).

$$\mathrm{2H^+ + 2e^- \rightarrow H_2} \tag{16.4}$$

The lower the pH, the faster corrosion can take place, because there is more H^+ in solution to accept electrons at the cathodic sites. (Remember, pH is a logarithmic scale.) Because most cooling systems operate in the pH range of 6.5 to 9.5, the reduction of H^+ does not occur. The primary cathodic reaction is the reduction of oxygen [Eq. (16.3)].

Secondary Reactions

These are the reactions that the primary corrosion products undergo in order to form stable corrosion products. The secondary reactions are critical in determining whether the oxide layers that make up the corrosion product deposits will retard or accelerate the corrosion process. Inhibitors can participate in these secondary reactions to form protective layers.

Ferrous Metals

Rapid conversion of ferrous ions (Fe^{+2}) to ferric ions (Fe^{+3}) is essential to the formation of stable, protective layers of ferric oxide on steel. The most stable form is FeOOH, commonly known as gamma iron oxide. The oxidation of the ferrous ions must occur very near the metal surface to form a protective film. If ferrous ions diffuse farther away from the surface before becoming oxidized, the resulting iron oxide, can form a loose, nonprotective deposit.

Corrosion inhibitors can have three common actions on an iron surface:

1. The inhibitor can directly oxidize the ferrous ions near the metal surface, to the stable gamma iron oxide film. Chromate and nitrite act as oxidizers to form gamma iron oxide, which prevents corrosion of steel.
2. The inhibitor can catalyze the reaction of oxygen with ferrous ions near the metal surface to form the gamma iron oxide film. Orthophosphate and alkalinity are examples of catalysts in the corrosion inhibition process.
3. The inhibitor can absorb onto the oxide surface and strengthen the film against chloride penetration. Molybdate works in this manner.

Copper Alloys

Two oxides of copper may be formed by corrosion reactions. The formation of cupric oxide layers is detrimental and will not prevent corrosion, while cuprous oxides are more protective. Cuprous oxides are less soluble and more stable than cupric oxides. Even though the cuprous oxide can reduce corrosion of copper, this oxide film is not as protective on copper as the oxides of iron are on steel. For copper, corrosion inhibitors that form a film on the surface provide the best inhibition of the dissolution of copper at the anode and transfer of electrons at the cathode. (See Chap. 19 on Cooling Water Treatment and Control.)

Galvanic or Electrochemical Series

Galvanic corrosion is a special form of the general corrosion reaction. This form of corrosion results when two dissimilar metals are connected and exposed to a water environment. One metal becomes cathodic and the other anodic, setting up a galvanic couple or galvanic cell. For example, when copper and steel are connected in water, steel becomes the anode, and copper is the cathode. The metal loss occurs at the anode, so the steel corrodes at a faster rate, and the copper is protected from corrosion. Galvanic corrosion can be relatively common in cooling systems, for example, this occurs when a brass sample valve is placed on a steel pipe without separation by an insulating coupling.

Corrosion rate in a galvanic couple is dependent upon two factors:

1. What metals are connected
2. Relative anodic to cathodic surface areas

A galvanic couple in solution creates an electrical potential difference between the two metals. The electromotive or galvanic series illustrates the magnitude of that difference (Fig. 16.3). A pair of metals that are far apart in this table will have a greater potential difference (hence faster corrosion rate) than two metals that are close to each other in the table. The metals near the cathodic end of the chart are considered passive or noble metals. The metals near the anode end of the chart are considered active metals.

The relative size of the anodic and cathodic areas determines the rate and type of corrosion. A larger cathode coupled to a small anode will cause higher corrosion and often pitting-type corrosion. A smaller cathode joined to a large anode will result in a lower corrosion rate and more general corrosion loss (Fig. 16.4). These area relationships hold true as long as other factors influencing the system (e.g., temperature, conductivity, oxygen concentration, velocity, etc.) are equal.

Another type of galvanic corrosion that occurs in cooling water systems are when ions of a more noble metal, such as copper in solution are "electrodeposited" on the surface of a less noble metal, such as steel or aluminum. This happens when the copper ions participate in the cathodic corrosion reaction and are reduced to copper metal on the surface. The copper ions take the place of oxygen in the cathodic reaction, as shown in Eq. (16.5):

$$\mathrm{Cu^+} + \mathrm{e^-} \rightarrow \mathrm{Cu^0} \tag{16.5}$$

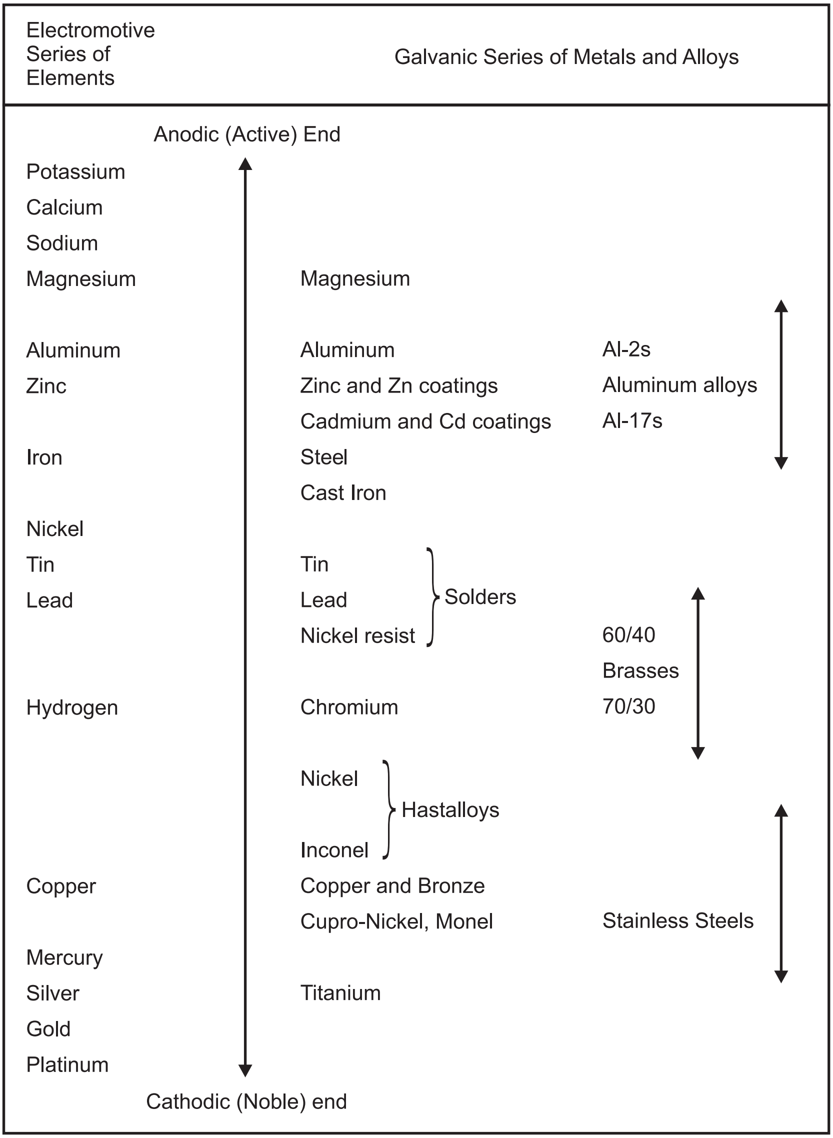


FIGURE 16.3 The electromotive series shows the relative potential of any two elements or metals in a galvanic couple.

If enough copper metal is plated onto a more active metal surface, localized galvanic corrosion can occur. Aluminum is particularly vulnerable to galvanic corrosion from copper in cooling water. Figure 16.5 shows an example of this type of galvanic couple from copper plated onto a mild steel corrosion coupon.

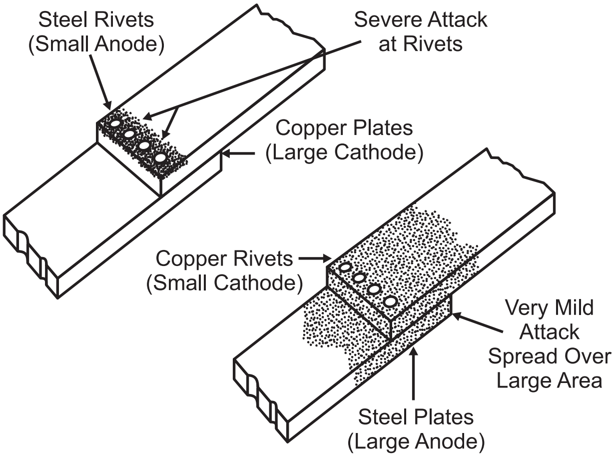


Figure 16.4 The rate of galvanic corrosion depends on the ratio of the anode area to the cathode area.

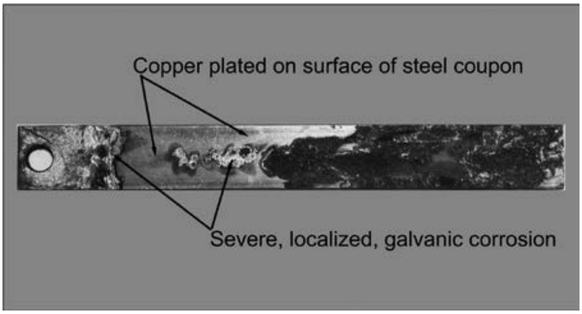


Figure 16.5 Example of galvanic corrosion due to the direct coupling of dissimilar metals. In this case, the galvanic couple is formed between the mild steel coupon and the electrodeposited copper on the steel coupon.

The Role of Oxygen in Corrosion

The oxygen concentration will affect the corrosion rate, either by increasing corrosion or by passivating the surface, which prevents corrosion. A low oxygen concentration causes a low corrosion rate, because the diffusion of oxygen to cathodic sites is limited. As the concentration of oxygen increases, diffusion increases, and corrosion rate increases. As oxygen concentration increases further, the corrosion rate may reduce again because the high oxygen concentration rapidly oxidizes ferrous ions near the metal surface to form a protective film. High oxygen concentration can accelerate the formation of dense, adherent passive films on the metal that diminish or even

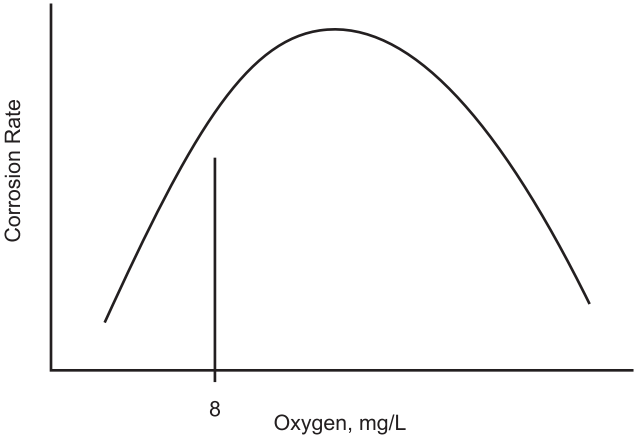


Figure 16.6 Effect of oxygen concentration on mild steel corrosion rate under cooling tower system conditions.

prevent further corrosion. Figure 16.6 shows the effect of oxygen on the corrosion rate in cooling water conditions.

The oxygen concentration of the water varies, depending on the type and characteristics of a cooling system. The constant aeration as the water passes over a cooling tower will maintain oxygen saturation. This provides enough oxygen to support corrosion in open recirculating cooling systems. In closed systems, generalization about the oxygen concentration is more difficult. The oxygen concentration will be depleted over time in a truly closed system (no leaks). The loss of oxygen happens faster at higher temperature in closed water systems. Closed systems with leaks or systems that have open storage tanks will never lose all the dissolved oxygen, unless the water temperature is over 180°F (82°C), where oxygen solubility is very low.

Polarization and Corrosion Rates

The rate of either corrosion reaction (at the anode or at the cathode) is reduced by polarization of the metal surface, which occurs in several ways. First, a passive film of metal oxides or corrosion inhibitor can slow down the anodic corrosion reaction (metal loss). In the case of iron, a passive iron oxide film will reduce the dissolution of Fe° at the anode. Second, if the oxygen concentration in the solution is low, the lack of oxygen at the cathode will reduce corrosion. A final example is that cathodic reaction products like hydroxide (OH^-) can remain at the metal surface, forming a layer that prevents further reduction of oxygen by electrons in the metal. Figure 16.7 shows how a layer of hydroxide ions can form on the cathodic surface from the reaction of oxygen and water with electrons from the metal. The net effect of the hydroxide ion layer is a reduction of corrosion rate.

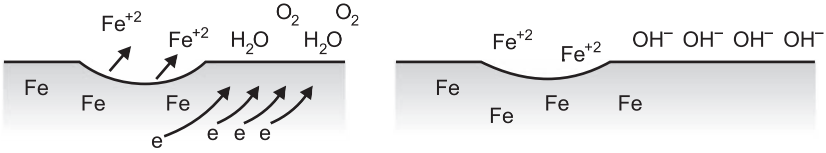


Figure 16.7 Polarization of the cathode by a concentrated film of hydroxide ions.

Removing or disrupting these anodic or cathodic barriers causes depolarization, and will restart the corrosion process. Several factors can lead to depolarization. One example is lowering the pH of the water, which increases the concentration of the hydrogen ions. These ions can then react with the hydroxyl ion formed at the cathode, removing the OH^- film and depolarizing the cathode. A lower pH will also increase the solubility of most anodic corrosion products and some cathodic inhibitor films. High flow velocity can also cause depolarization, promoting diffusion of ions or dissolved gases, both away from and to the metal surface. High velocity of water containing suspended material can erode a passive film from the metal surface. The net effect of depolarization is an increase in corrosion rate.

Passivity and Immunity

Immunity is the state in which a metal is more stable than oxides of that metal in a given environment. Metals that are immune to corrosion are called noble metals. Gold and platinum are examples of noble metals that are immune to corrosion in most normal environments.

Passivity is the state in which a metal forms a stable protective oxide layer on the surface, which prevents further dissolution of the metal. This passive oxide layer is formed by corrosion on a clean metal surface. The corrosion products are insoluble and rapidly form the passive film. The film acts as a barrier, separating the metal surface from the environment. For further corrosion to occur, the reactants must diffuse through the oxide film. Such diffusion is very slow or nonexistent, thus corrosion either markedly decreases or stops.

Passivity is essentially a condition on the metal surface where the corrosion rate is very low and a loss of chemical reactivity has occurred. Stainless steel is a good example of a metal that exhibits passivation in the presence of oxygen. The passive film is invisible and very thin, but significantly inhibits corrosion.

To be effective, a passive film must provide a barrier to both electron flow and diffusion of atoms and ions to and from the metal surface. An effective film must resist breakdown. The formation of a passive film is a dynamic process; the film can be broken down, and repassivation can occur. If the rate of breakdown exceeds the repassivation, corrosion can occur. If the breakdown is localized to small areas, pitting can occur. (Pitting corrosion is covered in more detail later in this chapter.)

Breakdown of the passive film can occur by chemical, electrochemical, or mechanical factors. Chloride ion in water can cause chemical breakdown of passive films. Mechanical breakdown can occur due to stress or abrasive wear, such as high-velocity water containing suspended solids. Inhibitor-created passive films can break down by these external factors, or by lack of program control. If the inhibitor level drops, passivation rates can decrease and corrosion rates increase.

Factors Influencing Corrosion

A number of parameters affect whether corrosion will occur, as well as the rate of corrosion itself. Adjusting system operation accordingly can significantly reduce corrosion. The more common and important factors will be discussed.

Water Chemistry

Water chemistry has a strong and varied effect on corrosion. The influence of dissolved solids on corrosivity is complex. The concentration and type of ion are both important. For example, some dissolved solids (carbonate and bicarbonate) reduce corrosion, while other aggressive ions (chloride and sulfate) typically increase corrosion by interfering with the protective film. Corrosivity does not increase at a linear rate with increasing total dissolved solids concentration (Fig. 16.8).

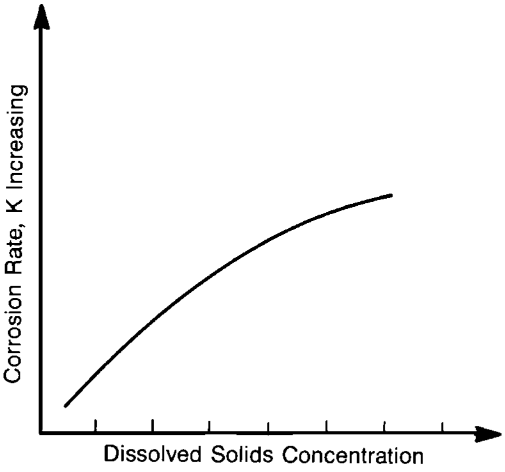


Figure 16.8 Influence of dissolved solids on corrosion rate.

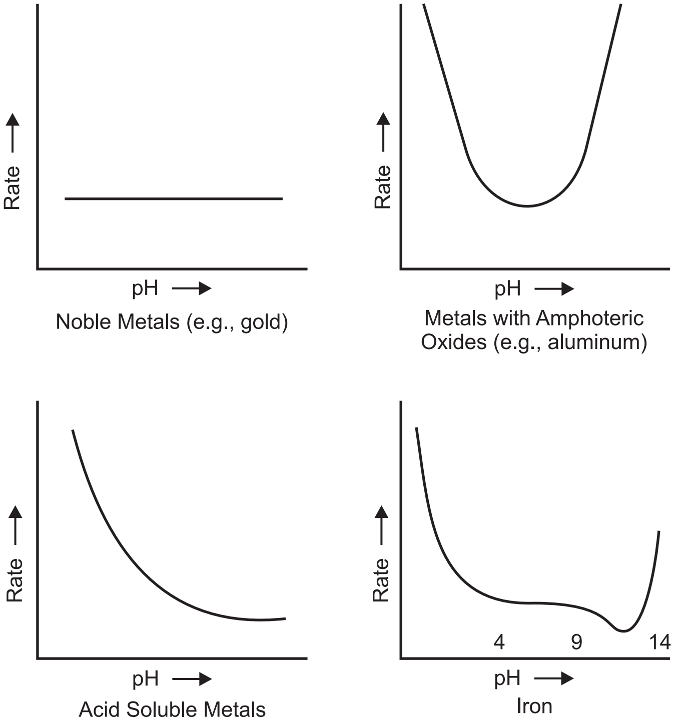


Figure 16.9 Variation in corrosion rate with pH for different metals.

Anything that increases solubility of the metal will increase corrosion. The pH of the water can have a dramatic effect on corrosion, and this effect varies with different metals. Figure 16.9 shows the effect of pH on four different metals. With most metals, acidic conditions are corrosive. The increase of hydrogen (H^+) in the water at low pH can dramatically increase the rate of the cathodic reaction, since H^+ is reduced at the cathode. The corrosion rate in acidic conditions will depend upon the alloy and the type of acid. For instance, oxidizing acids such as nitric will passivate stainless steel but will destroy carbon steel and yellow metals. Noble metals like gold will resist the corrosive effect of most acids. Amphoteric metals like aluminum and zinc corrode with both acid and base, and the corrosion rate increases at both ends of the pH spectrum. Chelating materials can increase corrosion on many metals by increasing the metal ion solubility.

Chloride and sulfate are aggressive ions that can increase corrosion rates. Chloride will attack the passive film on both steel and stainless steel. Chloride increases the solubility of ferrous ions and can prevent good film formation. Chloride ions play a strong role in ion concentration cells that can occur in crevices or under deposits, and chloride is a direct contributor to stress corrosion cracking of austenitic stainless steel. (Concentration cell corrosion and stress corrosion cracking are covered later in this chapter.) A key factor in diminishing the effect of chloride in cooling water systems is surface cleanliness. Minimizing deposition will help prevent ion concentration cell formation and allow the corrosion inhibitors to function more effectively, minimizing the impact of chloride on corrosion.

On the other hand, alkalinity in the water can have a very positive role in reducing corrosion. Alkalinity can reduce the rate of both the anodic and cathodic corrosion reactions. As an anodic inhibitor, alkalinity buffers the pH to regions where formation of ferrous hydroxide is favored. This ferrous hydroxide is an intermediate step to the formation of gamma iron oxide (FeOOH). Carbonate can participate in the anodic reaction by the formation of ferrous carbonate ion pairs in solution. These ferrous carbonate clusters can react with oxygen in solution to form gamma iron oxide under the right conditions. The reaction with oxygen is preferred, since the gamma iron oxide forms a passive film on the surface as shown in Fig. 16.10. Strongly passivating conditions result at pH around 9.0 to 9.2 under cooling system conditions. At lower pH, around 8.5, the system is not as strongly passivating. As a cathodic inhibitor, calcium carbonate can precipitate due to the locally higher pH at the cathode. This film can prevent the reduction of oxygen by preventing the electrons from migrating out of the metal. The formation of the cathodic film is dependent on the solubility of calcium carbonate in the system and at the surface. The solubility of calcium carbonate is a delicate balance, because too much precipitation will cause scale and too little calcium carbonate will allow corrosion to continue. Therefore, the anodic mechanism is more desirable for corrosion prevention.

Dissolved Gases

Carbon dioxide (CO_2) and dissolved oxygen (O_2) are the major gases of concern in cooling systems. Increasing the free CO_2 content in water reduces pH and increases corrosivity. In weakly buffered condensate in a steam system, this could produce low pH and corrosive water. However, in buffered water, like a typical cooling water system,

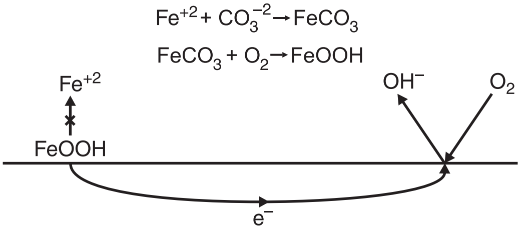


FIGURE 16.10 Alkalinity aids in the formation of gamma iron oxide.

the impact of the increased CO_2 is usually minimal. (Dissolved oxygen was covered earlier in this chapter.)

Hydrogen sulfide (H_2S) and ammonia (NH_3) are less frequently encountered gases, but both can increase corrosion of iron and copper alloys. Hydrogen sulfide is usually ionized as bisulfide and sulfide ions, which tend to depolarize the anodic area. Ammonia increases the corrosion rate of copper and copper alloys by forming soluble complexes with the copper. Ammonia can remove protective cuprous oxide or copper carbonate surface films.

Halogens and Other Oxidizers

Oxidizing agents, like chorine, can interfere with inhibiting films on metal surfaces. Oxidizers can act as depassivating agents by destroying a passive film on a metal surface. Halogens, particularly chlorine, can promote corrosion of copper and copper alloys. Chlorine can react with and strip the inhibitor film that may be created by azole-based copper corrosion inhibitors. The loss of the azole film will increase corrosion rates.

Temperature

As a rule, a temperature increase of 18°F (10°C) doubles the rate of most chemical reactions. Therefore, an increase in temperature increases the speed of corrosion, because the corrosion reactions proceed faster. In addition to increasing the rate of reactions, the oxygen diffusion rate also increases with increased temperature. Fig. 16.11 shows the relationship of temperature and oxygen concentration on corrosion rates.

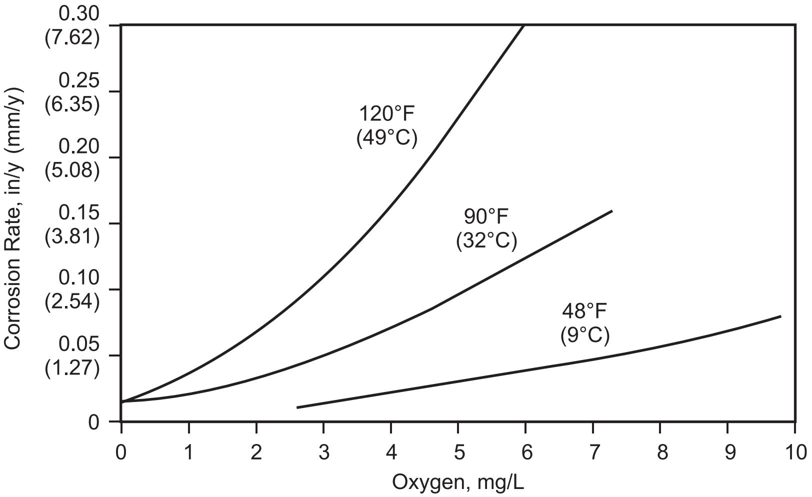


FIGURE 16.11 Effect of temperature on corrosion at different oxygen concentrations.

Flow Velocity

In general, corrosion will increase with an increase in water velocity, and corrosion normally becomes more uniform (general etch). However, the effect of flow velocity change is not always that simple. High and low flow rates can have both positive and negative effects on corrosion. Figure 16.12 depicts the general relationship between water velocity and the corrosion rate for steel.

Examples of negative effects that relate to Fig. 16.12 include:

- Erosion corrosion can occur at very high water velocity.
- Oxygen is carried to cathodic sites more effectively at high water flow rate, increasing the cathodic reaction rate.
- Low flow or stagnant conditions allow suspended material to settle onto the bottom of tubing and bottom surfaces of other components. This promotes under-deposit corrosion.
- At low flow, iron oxide deposits are generally loose and nonprotective.
- Tubercle formation on iron is often more severe in low-flow situations. This is a form of under-deposit corrosion.
- Biocides and inhibitors will not be replenished as rapidly at the metal surface when low flow exists. Control of microbial growth and corrosion protection is reduced under low-flow conditions.

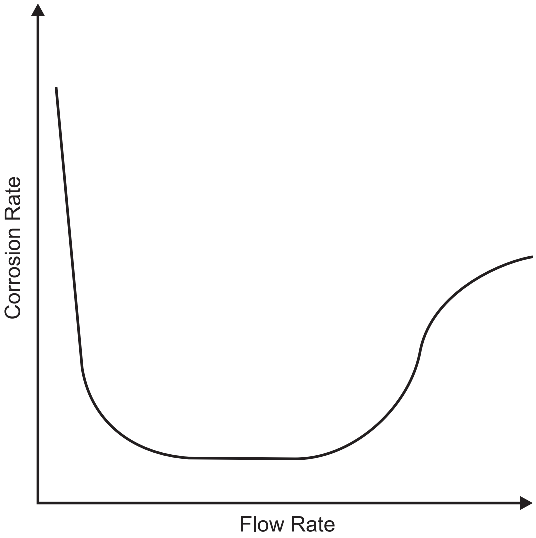


Figure 16.12 Both low and high water velocity can increase corrosion.

Positive effects of water velocity changes include:

- Increased velocity can decrease corrosion by replenishing corrosion inhibiting ions at the metal surface faster.
- Some metals and alloys, such as iron, aluminum, and stainless steel, rely upon oxygen to form a passive film that will inhibit corrosion. Increasing the water velocity will increase the oxygen supply available at anodic sites to speed the formation of protective oxide films.
- Proper water velocity and a good treatment program will help to keep metal surfaces clean, which aids corrosion inhibitor effectiveness and helps prevent under-deposit corrosion.

From a practical standpoint, the water velocity should be sufficient to keep the surfaces clean so that the corrosion inhibitors can function on the metal surface.

System or Spatial Configuration Factors

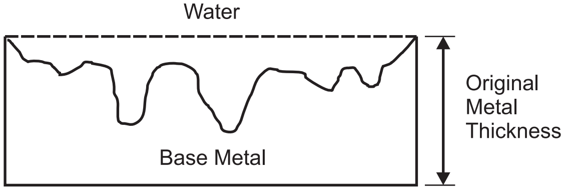
A variety of physical factors in the system can cause increased localized corrosion. Obviously, crevices created by poorly joined surfaces can lead to concentration cell corrosion, as discussed later in this chapter. Dead spaces or low-flow areas can create corrosion problems due to deposition, lower oxygen concentrations, or microbial growth that may exist in these areas. Places where water flow changes direction rapidly, or where a sudden pressure decrease occurs, can cause corrosion by erosion of the metal or the inhibiting film. Erosion corrosion is a process where the inhibiting film is repeatedly worn off and then reforms. This process eventually causes severe loss of metal thickness.

Deposits

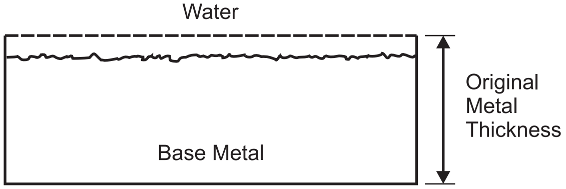
Most deposits generally have a negative effect on corrosion. Any type of deposit may cause under-deposit corrosion from the formation of differential oxygen or differential ion concentration cells. Deposits can harbor bacteria that can increase the deposition problem. Bacteria can influence corrosion directly by forming anaerobic environments for the growth of sulfate-reducing bacteria.

Types of Corrosion

There is a variety of ways to classify the different forms of corrosion. Corrosion can be classified by appearance of the corroded metal, the area corroded, or the mechanism of the corrosion process. The most common forms of corrosion will be covered. More detail and additional examples of types of corrosion can be found in *The Nalco Guide to Cooling Water Systems Failure Analysis*, 2nd ed. mentioned earlier in this chapter.



Localized / Pitting Attack



General Etch / Uniform Attack

Figure 16.13 Appearance of pitting and localized corrosion versus uniform corrosion.

Uniform Corrosion

Uniform or general corrosion happens when the anodic reaction (metal loss) occurs in a uniform manner on the metal surface. The anodic sites change location rapidly and are distributed over the metal surface. This type of corrosion loss is sometimes called general etch or general wastage, and is simply a progressive thinning of the metal (Fig. 16.13). In cooling systems, this form of corrosion may be experienced during an acidic pH excursion. The aggressive, acidic water will corrode the metal at all points on the surface, “etching” away the metal.

General corrosion is the most common form of corrosion experienced in industry. The thickness of cooling system piping is designed for an expected general corrosion rate, dependent upon the desired service life. Uniform corrosion can be reduced by the proper application of corrosion inhibitors, coatings, or cathodic protection. Thus, this is the least dangerous and most easily prevented form of corrosion. General corrosion is the most predictable and easily measured with corrosion coupons or continuous monitoring devices. (See Chap. 18 on Cooling Water Monitoring.)

Pitting Corrosion

Pits are generally defined as a cavity or hole where the surface diameter is equal to or less than the depth of the pit. Pits can be distributed across a metal surface or isolated to a given area. Figure 16.13 compares pitting metal loss with uniform metal loss. Pitting corrosion is a common result of breakdown of a passive film in a small, localized area. This localized area becomes anodic, and the remainder of the inhibited surface of the metal is the cathode. The corrosion rate can be very high, when the anode is small and the cathode is large. This type of pitting can occur on clean surfaces as well as surfaces with deposits. For example, in some aggressive environments, pitting will occur on clean stainless steel surfaces. Pitting is more dangerous than general corrosion because pitting can proceed more rapidly and is focused on discrete areas. This can result in system metal failure much faster and with less overall metal loss than general corrosion.

Pitting can occur very quickly if a treatment program is not controlled properly. Low dosage of an anodic corrosion inhibitor like nitrite can cause breakdown of the passive film on metal surfaces. Pitting corrosion will result if the breakdown of the passive film is in small areas compared to the size of the remaining inhibited metal surface. The small areas are active anodes, and metal loss can proceed rapidly due to the large inhibited surface, which is the cathode. This is why oxidizing, anodic corrosion inhibitors are referred to as "dangerous inhibitors." Control of dosage above a minimum value is essential to maintain the passive film.

Localized Corrosion

Localized corrosion can take many different forms that proceed by a variety of processes. Localized corrosion typically covers less than two-thirds of the metal surface. The most common forms in cooling water systems are tuberculation, under-deposit attack, and crevice corrosion. These types of localized corrosion are forms of concentration cell corrosion and all proceed by a similar mechanism, where the concentration of a given species in the water is different at the anode than at the cathode. The crevice or deposit helps to create and maintain the concentration difference. This illustrates the importance of treatment to both inhibit corrosion and keep the surfaces clean and free of deposits. Pitting may result from concentration cell corrosion that occurs under deposits, but localized corrosion sites may have larger openings than the depth of the corrosion site.

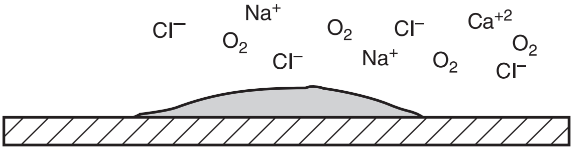
Concentration Cell Corrosion Mechanisms

If the concentration of a dissolved ion or molecule is different at two places on the metal surface, a concentration corrosion cell can occur. Surface deposits or crevices provide the conditions necessary for the formation of differential concentration cells. A crevice can form wherever two pieces of metal are joined. The crevice may be very small, even only a few thousandths of an inch (100 μm) wide, but this is large enough to fill the crevice with water for corrosion to occur. Surface deposits shield the metal from the bulk solution. Deposits on the metal surface or a crevice can create the conditions for concentration cell corrosion.

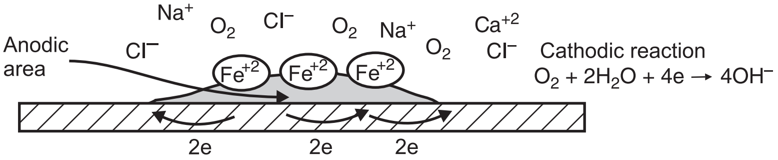
A variety of dissolved species can cause concentration cell corrosion:

- Dissolved oxygen
- Chloride or sulfate ions
- H^+ or OH^- ions (pH)

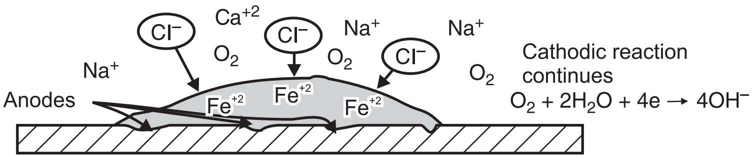
Since corrosion consumes oxygen in the under deposits or in a crevice, the concentration of oxygen in these locations will become lower than the oxygen concentration outside the deposit. Figure 16.14 shows



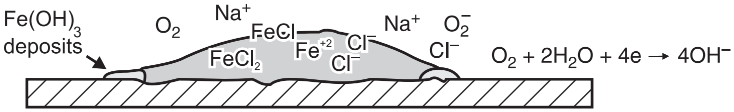
(a) Debris settles on a metal surface.



(b) Oxygen can reach metal only at the open surface.



(c) Oxygen continues to depolarize the cathodic area while chloride diffuses into the porous deposit.



(d) The iron within the deposit remains soluble as Fe^{+2} in the absence of O_2; and corrosion increases as ionic strength in the deposit increases.

Figure 16.14 The sequence of steps in the formation of an oxygen concentration cell due to deposit on a steel surface in oxygenated water.

the formation of a differential aeration cell under a deposit. The metal surface beneath the deposit becomes anodic, metal loss occurs, and a concentration corrosion cell is initiated. The anodic and cathodic reactions are the same reactions that occur in general corrosion, but here the two reactions are separated on the metal surface by deposits.

The corrosion under the deposit or in a crevice becomes progressively worse as metal ions are released into the solution at the anode. The solution at the anodic site takes on an excess positive charge. This positive charge will attract anions like chloride to maintain electroneutrality of the solution. If the deposit is semipermeable, this barrier inhibits the mixing of anodic and cathodic reaction products, but allows some species such as chloride and sulfate ions to pass through (Fig. 16.15). As the chloride and sulfate ions increase, more extreme corrosion can occur. Metal chlorides or sulfates can cause hydrolysis of water to produce acids under the deposits or in the crevice, further accelerating the attack. The crevice may become increasingly acidic as time progresses (pH around 3). The potential difference between the anode and cathode continues to increase, which will accelerate the corrosion rate. Thus, the conditions under the deposit can become autocatalytic and self-sustaining.

In summary, deposits can aggravate localized attack, which starts as normal corrosion, but is compounded by various concentration cell corrosion mechanisms. Sometimes, microbial involvement may cause additional corrosion. The rate of differential concentration cell corrosion is proportional to the difference in concentration of the oxygen and ions under the deposit and the concentration of those species found in the water around the deposit. Because these concentration cells are shielded by deposits of corrosion products over the cell, not even the most effective corrosion inhibitors can get through to properly protect the metal surface. This emphasizes the importance of keeping water systems free of deposits.

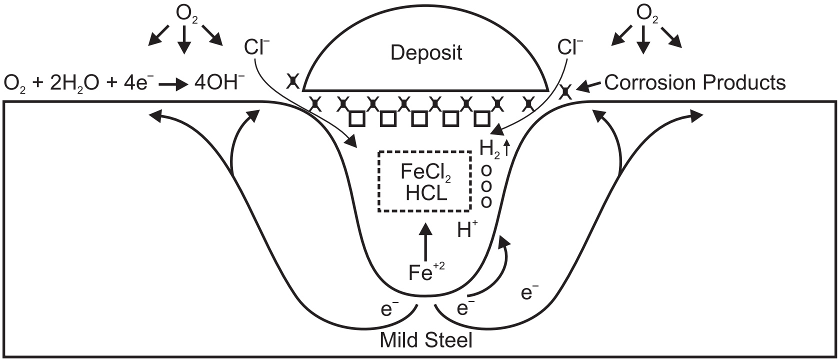


FIGURE 16.15 Chloride ion concentration cell under deposits can produce acidic conditions that accelerate corrosion.

Minimizing the concentrations of aggressive ions like chloride and sulfate by controlling concentration cycles can help to reduce concentration cell corrosion. However, this form of corrosion may occur as long as aggressive ions are present in the water. There is no safe limit for chloride and sulfate in solution, because these ions participate by a concentration mechanism. As the concentration of aggressive ions decreases, the severity of attack will decrease, but concentration cell corrosion can still occur at low chloride levels.

Tuberculation

Tuberculation is a unique type of under-deposit corrosion, where mounds of corrosion products cover localized regions of metal loss. Tubercles form on non-stainless steels and cast iron, when surfaces are exposed to oxygenated water. Soft water with high bicarbonate alkalinity stimulates tubercle formation, as do high concentrations of sulfate, chloride, and other aggressive anions. Tubercles can grow quite large and plug pipes, diminish water flow, and increase pumping costs. Tubercles cause localized corrosion, but generally do not cause pitting corrosion. The diameter of the corroded area is often much larger than the depth. In some cases, extensive tuberculation can appear like general corrosion after the surface is cleaned. In severe cases, tuberculation can cause penetration of the pipe or exchanger tube.

Corrosion under tubercles can occur by an oxygen concentration cell or by chloride and sulfate ion concentration cells that increase the anodic reaction rate. Anions can cause an acidic solution to form inside the tubercle, which helps to maintain the fluid-filled cavity. This is illustrated in Fig. 16.16. In addition, because of the reduced

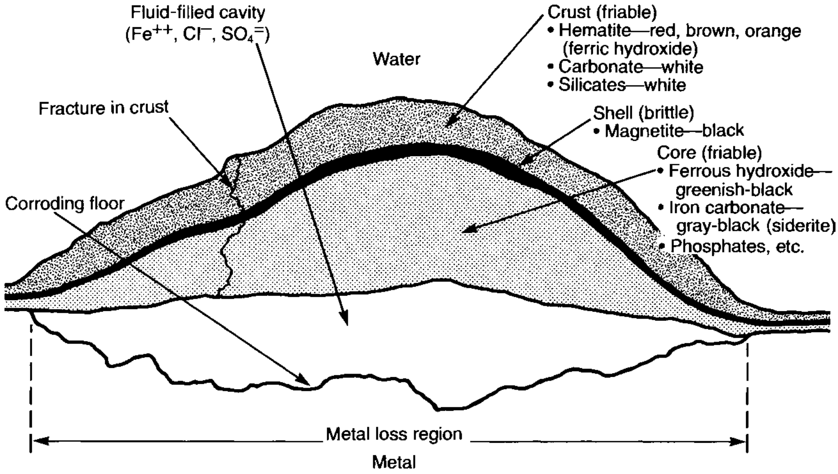


Figure 16.16 Cross section of a typical tubercle and the composition of the layers.

Figure 16.17 Example of tubercles that form long tubes in the direction of flow in a pipe.

oxygen concentration and elevated sulfate levels, sulfate-reducing bacteria (SRB) can grow inside tubercles. This type of corrosion is rather common in systems that are not properly treated. Identifying tubercles is important so that corrective actions can be taken. Examples of tubercles in a water supply pipe and the damage tuberculation causes are shown in Figs. 16.17 and 16.18, respectively.

Alloys

Under-deposit corrosion that occurs on alloys often involves differential concentration cells containing aggressive anions. The most common example is chloride concentration attack on stainless steel.

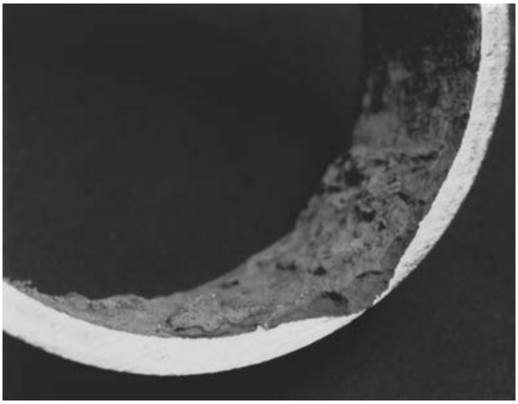


Figure 16.18 Example of a wide but deep corrosion site under a tubercle that actually penetrated this pipe.

Figure 16.19 Example of severe localized corrosion in a 316 stainless steel heat exchanger tube that occurred under deposits on the tube surface.

The low pH that can occur in concentration cells under deposits will increase pitting or localized corrosion. The deposits can be silt, sand, oil, process leaks, biomass, scale precipitates, metal sulfides, or manganese dioxide. Deposits that are more water permeable will produce the most severe attack. Any location in a system can experience deposition. Areas with low or intermittent water flow, such as shell-side heat exchangers, service water systems, sumps, or exchanger head boxes, may be problem areas.

Concentration cells on stainless steel cause depassivation of the metal surface. The concentration of aggressive ions causes breaks in the passive surface, and corrosion attack can be intense and localized, as shown in Fig. 16.19. Loss of metal below the surface can be much greater than metal loss on the surface.

In utility condensers that are made of copper alloys, pitting under manganese deposits can be a problem. This is particularly common in once-through condensers, where the supply water contains soluble manganese. Chlorination of the water or the action of dissolved oxygen can oxidize the manganese to insoluble forms that precipitate on the condenser tubing. Deposition in the condenser is increased when water is chlorinated immediately preceding the condenser inlet or water box. Manganese dioxide deposits are more noble than the tube metal, and promote corrosion due to galvanic effects (Fig. 16.20). This type of corrosion will occur on 304 stainless steel as well.

Microbiologically Influenced Corrosion

Even the name of this type of corrosion has created controversy. Some think the corrosion is “induced” by the presence of biological organisms, while others think corrosion is only “influenced” by them. This

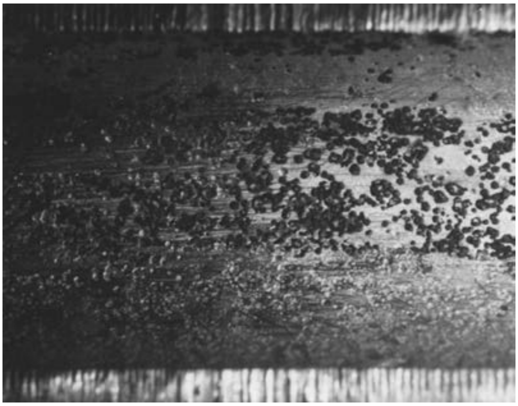


Figure 16.20 A 90:10 cupro-nickel condenser tube with small pits under the dark manganese-rich nodules on the surface.

is another "chicken and egg" situation. Either case may be correct depending on the organism and conditions. Microbiologically Influenced Corrosion (MIC) is now accepted to be corrosion that is either *actively induced* or *passively influenced* by microbial organisms.

Microorganisms can contribute to corrosion in different ways. In any case, the basic electrochemical corrosion reactions are still part of the process. Some microbial organisms will produce byproducts that actively accelerate corrosion or produce new corrosion sites. All microbial organisms can create deposits that form sites for under-deposit corrosion from concentration cell mechanisms. Pitting or localized corrosion is often a result of MIC. The interior of the corrosion site is usually hemispherical in shape and characteristically smooth, often with concentric rings on the metal surface. Pits are often more smooth on more corrosion-resistant metals. The metal surface beneath the corrosion products is often bright or shiny. Pits can also undercut the surface to give a characteristic profile when viewed in cross section, as in Fig. 16.21.

The key organisms that participate actively in corrosion fall into four main types: sulfate reducers, acid producers, metal depositors, and slime formers. The most common form of MIC involves SRB. These anaerobic bacteria grow in the absence of oxygen. SRB may survive when oxygen is present but do not actively grow. SRB occur in most natural waters and in soil or sediments. *Desulfovibrio*, *Desulfomonas*, and *Desulfotomaculum* are three common genera of sulfate reducers. Sulfate (SO_4^{-2}) or sulfite (SO_3^{-2}) must be present for them to actively grow. The metabolic process of these bacteria reduce sulfate to sulfide (S^{-2}). Because SRB are anaerobic bacteria, sulfate reducers will be found more predominately under deposits. SRB can be determined by microbial analysis. Corrosion sites are often filled

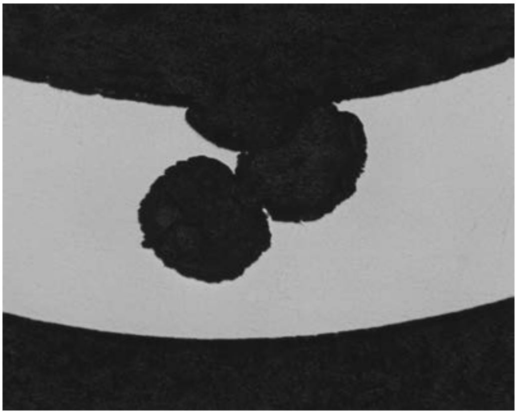


Figure 16.21 Example of pits caused by MIC that partially undercut the surface of a 316 stainless steel tube.

with black corrosion products containing iron sulfides. If SRB are found in a recirculating water sample, this could mean larger quantities are present under deposits in the system, and indicate potential problems.

A variety of mechanisms has been proposed to explain how SRB organisms accelerate corrosion under anaerobic conditions:

- Direct depolarization of the cathodic surface by removal of molecular hydrogen.
- Precipitation of ferrous sulfide at the anode. Ferrous sulfide is highly cathodic to metallic iron, and creates a galvanic cell.
- Creation of a highly corrosive pH (possibly <3) under deposits because of H_2S and other metabolic byproducts, typically organic acids.

Other bacteria can produce acid, either organic or inorganic. Regardless of form, the acid will reduce the pH, which accelerates corrosion. *Thiobacillus thiooxidans* and *Clostridium* are often linked to accelerated corrosion on steel. These are both anaerobic bacteria and survive best under deposits. *Thiobacillus* will oxidize sulfide to sulfate and may support the action of SRB deeper inside the tubercle. *Clostridia* produce short-chain organic acids that can be quite aggressive to steel.

Metal-depositing bacteria can oxidize ferrous iron to ferric iron, producing ferric hydroxide in normal cooling water conditions. Some can also oxidize manganese deposits. The ferric hydroxide produces a loose, poorly protective deposit that creates conditions for under-deposit corrosion and tuberculation. *Gallionella* and *Sphaerotilus* are two forms of these bacteria.

Most slime forming bacteria produce secretions of extracellular polymers and other metabolic by-products. The slime layers can contribute to corrosion both actively and passively. First, the bacteria consume oxygen, creating conditions for differential aeration cells. The slime layers form an occluding deposit that can contribute to both differential aeration and differential ion concentration cells. These deposits can also provide sites for anaerobic bacteria to live under the slime layer.

Stress Corrosion Cracking

Very small cracks can form in metal under stress that is exposed to a specific corrosive species, like chloride. This failure is called stress corrosion cracking (SCC). Both stress and corrosion processes are necessary and critical factors for SCC to occur. These two processes interact synergistically to produce cracks in the metal. The cracks start on the surface and grow in response to the stress and perpendicular to the direction of the stress. The cracks may be longitudinal along the length of the pipe or transverse around the pipe circumference. Examples are shown in Figs. 16.22 to 16.24.

The first critical factor necessary for SCC to occur is a stress in the metal. An externally applied tensile stress or a residual stress from the manufacturing process can promote SCC. Examples include stress from thermal expansion or contraction, pressure, and service loads. Internal, residual stresses may be locked into the metal during fabrication by rolling, drawing, shaping, welding, or installation.

The second critical factor for SCC is the presence of a specific corrodent species in the water. A given alloy will be susceptible to SCC only when a specific corrodent is present. Stainless steel (300 series)

Figure 16.22 Example of stress corrosion cracking on stainless steel—longitudinal crack.

Figure 16.23 Example of stress corrosion cracking on stainless steel—transverse crack.

Figure 16.24 Example of severe stress corrosion cracking on a stainless steel pipe.

will crack when exposed to chloride but not in the presence of ammonia. Figure 16.25 shows the nature of a stress crack in stainless steel exposed to water containing chloride. Brasses will crack in the presence of ammonia but not with chloride. In some cases, the concentration may not need to be very high, but in others, very high concentrations may be required.

SCC can be influenced by flow, alloy composition, concentration of corrodent, temperature, time, pH, presence of oxidizing agents, and the presence of deposits or crevices, which may concentrate corrosive agents. SCC can occur in a continuum from a high stress in a

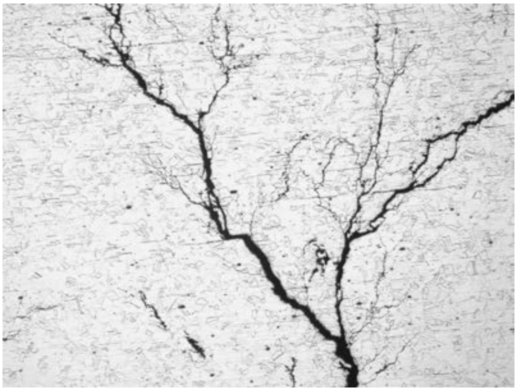


Figure 16.25 Stress corrosion cracking showing the typical branching of the crack.

mildly corrosive environment to a mild stress in a highly corrosive environment, depending on all of the factors involved. Certain alloys have a temperature requirement for cracking to occur.

Largely, proper design and good fabrication procedures should produce equipment, piping, or structures free of internal stresses. For example, heat treatment after fabrication (stress relief annealing) allows the crystalline structure of the metal to free itself of internal stresses. Even large process vessels may be stress relieved to guard against stress corrosion cracking.

Much has been discussed about the concentration of the corrodent in recent years. SCC can occur at concentrations of specific corrodents of 10 mg/L or less, depending on the temperature. A concentrating mechanism may increase the rate or tendency for SCC, but the concentrating mechanism is not necessary for SCC to occur. The inability to accurately estimate the concentration of a corrodent needed for SCC is a key reason predicting SCC is difficult.

CHAPTER 17

Cooling Water Biology

Bacteria are everywhere around us, in the water, air, and soil. Our bodies contain a wide variety of bacteria, some of which are useful, some are harmful, and some are just "along for the ride." If the bacterial population changes or grows out of normal proportion, the result is an infection. Just like our bodies, cooling systems are an ideal environment for bacterial growth. However, the cooling system can do nothing to control bacterial population growth without intervention by those who control the system. Therefore, the types of organisms that grow in cooling water systems and the impact of the growth and multiplication of the organisms must be understood to maintain proper system performance.

Microbial fouling is a central problem in cooling water systems (Fig. 17.1). Central because microbial slime can cause fouling from suspended material, corrosion, and scale formation faster than many other conditions in cooling water systems. Cooling water systems can be plagued with a variety of biological organisms. Bacterial slimes and algae come to mind first, because they are seen when heat exchangers are opened or on the deck of a cooling tower. Algae can also be a problem in large impounded lakes used for electric utility plant cooling. Other microorganisms like fungi or protozoa are sometimes found in cooling systems. Pathogenic organisms like *Legionella* bacteria can also be a problem. Finally, larger organisms like clams and mussels can cause macrofouling of once-through cooling water systems or pump intakes on lakes or rivers. This chapter will cover microbial fouling and macrofouling. *Legionella* will be covered in Chap. 20. Control methods to minimize biological growth in cooling water systems are covered in Chap. 19.

Sources of Biological Problems in Cooling Water Systems

Microorganisms enter cooling water systems from two primary sources. One is the makeup water in which microorganisms are already present. The concentration of organisms will vary depending

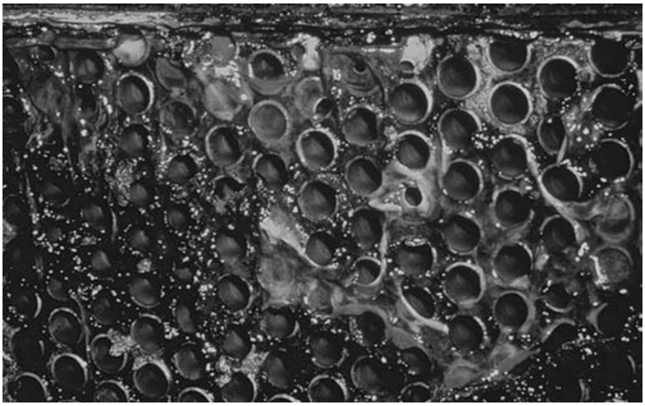


Figure 17.1 Bacterial slime on an exchanger tube sheet.

on the source of makeup water. A river or lake may contain large amounts of biological growth, depending on the condition of that water source. A potable water source should have a very low bacterial population, but is not sterile. Some freshwater or salt-water sources may contain clams, mussels, or other macroscopic organisms that can grow in cooling systems and cause serious problems. The second source is via airborne microorganisms that are blown into the cooling tower. Windblown dust from soil or other dirt will contain a variety of organisms. Bacteria that can form dormant cysts or spores, will survive stressful environmental or very dry conditions then revive and grow once they are in a suitable environment. So the presence of biological organisms cannot be prevented, but the growth and subsequent cooling system problems caused by biofouling must be controlled to a level where problems do not occur.

Consequences

The consequences of biological growth in cooling systems are varied, depending on the type of organism and system involved. Heat transfer loss by bacterial slime in heat exchangers is the first consideration. Microbial slime, like other fouling materials, reduces the efficiency of heat transfer. In fact, microbial slime is more insulating than other common deposits (Fig. 17.2). Heat transfer reduction can limit the efficiency of a process, affect the quality of the product, cause increased maintenance cost, or even shut down a process.

Another critical problem of biofouling is under-deposit corrosion. Certain organisms, for example sulfate-reducing bacteria, generate corrosive hydrogen sulfide, which can cause severe pitting on metal surfaces (Fig. 17.3). Slime can accelerate corrosion by depositing on

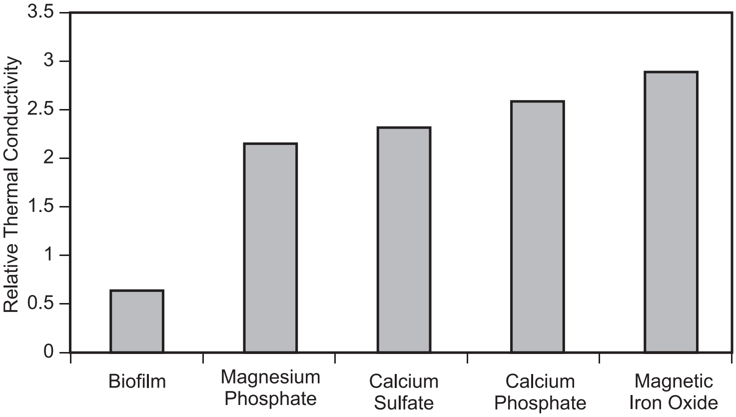


Figure 17.2 Biofilms have much lower thermal conductivity than other types of heat exchanger deposits.[1]

Figure 17.3 A pit caused by sulfate-reducing bacteria that perforated a carbon steel pipe at a weld-backing ring.

the metal and preventing protective film formation. In addition, slime layers can also cause under-deposit corrosion by the formation of concentration cell corrosion. (See Chap. 16 on Corrosion for more information on concentration cell corrosion.) These problems can lead to penetration of heat exchangers, causing product contamination or increased fouling by loss of product into the cooling water.

Other problems include a reduction of tower performance from plugged water distribution nozzles on the deck of a cooling tower by algae. Flow reduction in pipes can be caused by bacterial fouling and

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[1] Zelver N., Characklis W., Roe F., Annual Meeting of the Cooling Tower Institute Paper TP239A, CTI (Cooling Tower Institute), Houston, U.S., 1981.

can be a critical problem resulting from macrofouling in once-through cooling or in water intakes on oceans, lakes, or rivers. Larger organisms like clams and mussels cause macrofouling. The costs of macrofouling are estimated to be in the billions of dollars worldwide due to the high cost of either treatment or mechanical removal. Finally, material degradation, such as fungal deterioration of wood in cooling towers can cause serious structural or performance problems.

The sticky slime formed by bacterial deposits can trap other deposits, making the deposition problem worse. Slime masses provide excellent sites for the deposition of other foulants. Other microorganisms and suspended solids can add to existing fouling deposit. Slime on heat exchangers can cause or accelerate the rate of scale formation. When deposits form, heat transfer is reduced, and surface temperature increases. This temperature increase can result in precipitation of inversely soluble minerals like calcium carbonate or calcium phosphate. Bacteria can degrade some treatment chemicals, rendering them ineffective. If an inhibitor is degraded by microbial digestion, this could result in scale formation or corrosion. This causes possible production cutbacks and higher energy cost. This is why microbial fouling is placed at the center of the triangle representing the connection between the four problems of cooling water systems—corrosion, scale, fouling, and microbial growth. (See Fig. 15.1 in Chap. 15.)

Microorganisms Found in Cooling Systems

Bacteria, fungi, algae, and protozoa are the most common microorganisms found in cooling systems. Table 17.1 gives an overview of common organisms in these four groups. These organisms are the ones frequently associated with problems in cooling water systems. The classification is not strictly based on the biological classifications like order, family, genus, and species, etc., but combines this with metabolic processes of the organisms, and the types of problems that the organisms cause.

The presence of many different types of organisms in a system is a sign that the system is hospitable to growth. Diversity is an indication that a system may be out of control, as many microorganisms thrive on the by-products of others. As total disinfection is usually not possible, a key concept in microbiological control is to manage the system to reasonable microorganism levels and minimize the diversity.

Bacteria

Bacteria, the largest group of troublesome organisms, cause the most varied problems. Nalco groups bacteria commonly isolated from cooling water systems into four classes: aerobic slime formers, anaerobic

Classifications	Description	Common Problems
Bacteria		
Aerobic slime-forming *Pseudomonas* Pigmented Mucoids *Enterobacter* *Spores*	Sticky, gooey, masses usually colored by suspended solids or corrosion products.	Fouling Produce conditions for growth of anaerobic corrosive bacteria Produce acids Reduce heat transfer efficiency
Anaerobic corrosive *Desulfovibrio* *Clostridium* Facultative	Black appearance. Rotten egg odor (H_2S). Grow best under slime or other deposits and in low-flow areas.	Corrosion pH reduction
Iron-depositing *Sphaerotilus* *Gallionella*	*Sphaerotilus* can be white or rust-colored, whereas *Gallionella* is always rusty. Stringy, slippery; often forms voluminous red deposits.	Insoluble iron deposits Under-deposit corrosion
Nitrifiers	Produce acids in systems contaminated with NH_3.	pH reduction Corrosion due to inhibitor depletion
Fungi		
Molds *Aspergillus* *Penicillium* *Trichoderma*	Stringy, gooey, masses typically on wooden areas. Usually white or colored by system contamination.	Wood decay and fouling
Yeast *Torula* *Rhodotorula*	Leathery or rubbery; resembling mucus.	Fouling
Algae		
Oscillatoria *Chlorococcus*	Found living only in sunlight or source of light. Loose, slimy, rubbery. Often green or brown.	Plugging of distribution deck holes Food for slime-forming bacteria

Table 17.1 Typical Microorganisms That Can Be Found in Cooling Systems and the Problems Associated with Them

Classifications	Description	Common Problems
Protozoa		
Amoeba Ciliates	Larger, single cell organisms, up to 0.04 mils (1 mm). Move under own power. Use bacteria, algae, and organic matter as food. Some can form cysts.	Usually indicate severe microbial contamination in system. Certain protozoa can host *Legionella* bacteria.

Table 17.1 Typical Microorganisms That Can Be Found in Cooling Systems and the Problems Associated with Them (*Continued*)

corrosive bacteria, iron-depositing bacteria, and nitrifiers/denitrifiers. Table 17.1 lists the bacteria, in addition to other organisms, normally encountered in cooling water systems. These microorganisms have been selected for discussion because they are the ones frequently associated with problems in cooling systems. Each group has its preferred environment and thrives in specific areas of a water system.

Aerobic Bacteria

A wide variety of aerobic bacteria commonly is found in cooling water systems. These bacteria require oxygen, so they are found in aerated waters in most cooling systems. These bacteria are metabolically diverse and can adapt rapidly to conditions, so that they can grow anywhere in the system. The most troublesome aerobes often are those that produce slime layers (Fig. 17.4). Cell walls in many microorganisms are covered with extracellular polysaccharide. In some cases, microorganisms are capable of producing large amounts of extracellular polysaccharides resulting in slimy deposits. These

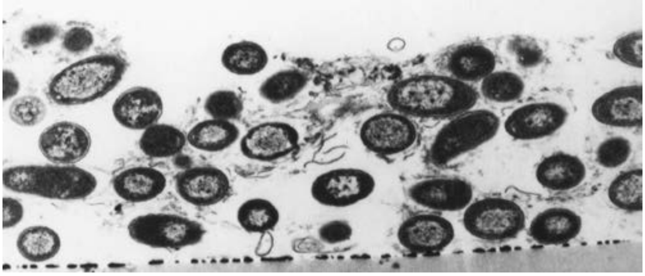


Figure 17.4 Example of biofilm. The bacterial cells are separated by the extracellular polymer that forms the slime that helps them stick to surfaces. Organisms are *Pseudomonas aeruginosa* at 7000×.

slime-encased cells attach to the available surfaces, reproduce, form additional slime, and develop into bio-deposits or biofilms. Biofilm formation and problems are discussed later in this chapter. The most common slime formers in cooling water systems are *Pseudomonas*, Pigmented, Mucoids, and *Aerobacter*. Of these, *Pseudomonas* is usually the most troublesome.

Some bacteria can be more harmful or indicate problems in cooling systems. *Enterobacter* is a type of coliform bacteria that is commonly found in sewage, and presence of *Enterobacter* in cooling water systems can indicate wastewater entering the system. *Legionella* bacteria are a potential threat to the health of individuals near a cooling tower. Chapter 20 covers *Legionella* in greater depth.

Anaerobic Corrosive Bacteria

Anaerobic bacteria are commonly found in both open and closed cooling water systems. Anaerobic bacteria do not require oxygen and obtain energy from reactions other than the oxidation of organic substances. Since anaerobes do not need oxygen, they are found in oxygen-deficient areas, such as under deposits, in crevices, and in sludge in tower basins. Several types of anaerobic bacteria cause corrosion of metal surfaces, such as sulfate-reducing bacteria (SRB). They obtain energy by reducing the ever-present sulfate ion to hydrogen sulfide (H_2S), a corrosive gas when dissolved in water. Some anaerobic bacteria produce organic acids as by-products of growth. These acids can also cause corrosion of some metal surfaces in cooling systems.

Desulfovibrio is the most notorious species of the sulfate-reducing bacteria. These organisms are widely found in wells, rivers, lakes, marsh soil, and in general, anywhere anaerobic conditions exist. *Desulfovibrio* require an oxygen-free environment to thrive. *Desulfovibrio* can survive for extended periods in a semi-dormant stage in the presence of oxygen. This allows them to move out of anaerobic environments and find new locations to inhabit. Other anaerobes such as *Clostridia* and facultative bacteria (those that can grow either with or without oxygen) also generate hydrogen sulfide from organic sulfur sources such as decaying algae.

The specific ways that SRB affect corrosion processes were covered in Chap. 16 (Cooling System Corrosion). The net effect is either initiation or acceleration of pitting corrosion on most metal surfaces, such as mild steel, aluminum, and stainless steel. Corrosion attributed to these anaerobes is always manifested as localized corrosion or pitting. The corrosion can cause penetration of the metal if allowed to proceed. Evidence of sulfate reducers is the unique, hemispherical pit etched on the metal surface, sometimes in the form of concentric rings (Fig. 17.5). Black deposits of iron sulfide in the bottom of the pits are also evidence of sulfate-reducing bacteria.

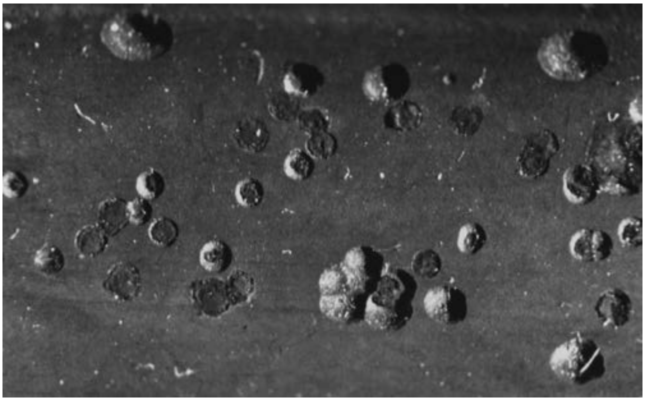


Figure 17.5 Smooth, hemispherical pits, often found in clusters or concentric rings are characteristic of sulfate-reducing bacteria.

Iron-Depositing Bacteria

These bacteria occur in water high in soluble, ferrous iron (Fe^{+2}), such as ground water, or beneath deposits on corroding iron or steel. Iron depositors convert ferrous ions to insoluble ferric hydroxide or oxide, which becomes part of the slimy, sticky sheath around the cell. These bacteria form deposits and accelerate corrosion rates, which produce additional soluble iron, further increasing the population of iron depositors in the system (Fig. 17.6).

Figure 17.6 Iron-depositing bacteria within tubercles contributed to the voluminous iron oxide deposition in this steel distribution pipe.

Two important species of iron-depositing bacteria in cooling water are *Gallionella* and *Sphaerotilus*. Both species can use soluble iron as an energy source. These microorganisms can live under low oxygen conditions or at interfaces between anaerobic and aerobic conditions. The iron deposits created by iron-depositing bacteria cause fouling and concentration-cell corrosion, as well as conditions under which anaerobic bacteria flourish.

Gallionella grow best in low oxygen conditions, for example, in water wells. These are environments where ferrous iron is not susceptible to chemical oxidation at neutral pH as occurs in aerated waters. *Gallionella* can use only soluble iron as an energy source, and the iron oxide formed is deposited within an outer sheath that has a spiral appearance when observed under the microscope (Fig. 17.7). The sheath containing the iron oxide then tends to deposit as a foulant in cooling water systems.

Sphaerotilus can use either organic nutrients or ferrous ion as an energy source. The effect of these bacteria on cooling water systems differs slightly from *Gallionella* because iron is not always present in deposits formed by *Sphaerotilus*. In these instances, *Sphaerotilus* will be white. *Sphaerotilus* has a distinct microscopic morphology, as shown in Fig. 17.8. The cells look like a row of train cars and are found primarily in once-through systems. Since *Sphaerotilus* and *Gallionella* grow best in low oxygen environments, these two bacteria are not often found in open recirculating cooling systems.

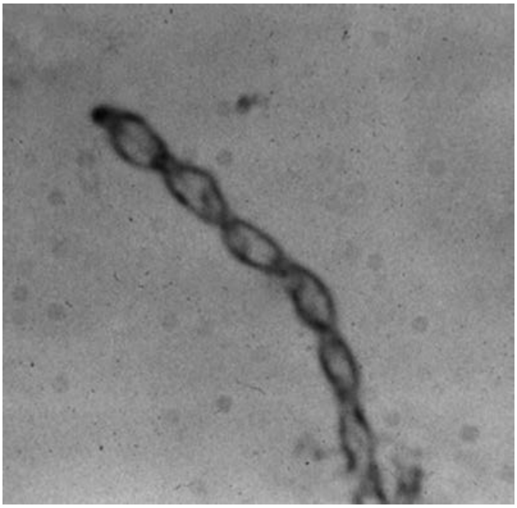


Figure 17.7 *Gallionella* are one type of iron-depositing bacteria (1000×).

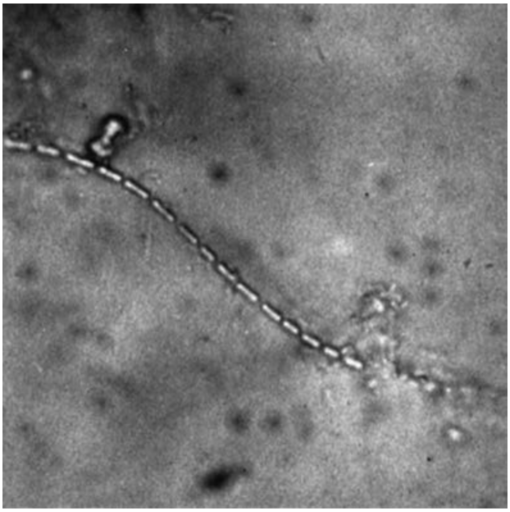


Figure 17.8 *Sphaerotilus* are another type of iron-depositing bacteria (400×).

Nitrifiers/Denitrifiers

Bacteria capable of deriving energy through the oxidation of nitrogen-containing compounds are commonly called nitrifying bacteria. Biological oxidation occurs in a variety of ways with different reactants and products. Organisms capable of oxidizing ammonia to nitrite are termed nitrosifiers, but are often referred to as nitrifiers. However, true nitrifiers are organisms that convert nitrite to nitrate. In cooling water systems, *Nitrosomonas* and *Nitrobacter* are the most common nitrifiers. Nitrogen fixing bacteria can convert molecular nitrogen to ammonia.

The nitrosifiers are most often found in open systems where ammonia contamination is possible. The oxidation of ammonia by bacteria produces nitrite. A pH drop caused by the conversion of ammonia to nitrite is often the clue to presence of nitrosifiers. If nitrifiers are also present, nitrate can be the final product.

Both nitrifiers and denitrifiers can exist in closed cooling water systems that are treated with nitrite-based corrosion inhibitors. Nitrifiers can deplete the nitrite-based inhibitor by converting nitrite to nitrate in oxygenated closed systems. This nitrification process produces nitric acid, so the action of nitrifiers in cooling water is generally associated with a drop in pH and an increase in nitrate levels. Corrosion can be caused by both the loss of nitrite and the production of acid.

Denitrifiers can be a common cause of denitrification in closed cooling systems. Denitrification is the process where microorganisms convert nitrate or nitrite to nitrogen gas. Denitrification is an anaerobic process and most relevant in tightly closed cooling water systems with nitrite treatment. The most common denitrifiers in cooling water systems are species of *Pseudomonas,* which are facultative anaerobes. These bacteria live in aerobic environments and use oxygen to grow but are adaptable to anaerobic conditions and use nitrite as a source of energy. If nitrite loss occurs in closed cooling water systems, denitrifiers or nitrifiers should be considered as a possible reason for the depletion.

Clostridia and blue-green algae are examples of nitrogen fixing organisms. Dissolved molecular nitrogen in water can be converted to ammonia by either an aerobic or anaerobic process. The ammonia that is produced can promote the growth of other organisms in the water.

Algae

The thick, greenish layers of slime on a cooling tower deck or floating on a cooling pond are often algae. Algae need sunlight to grow, and therefore are found on open surfaces of a tower, ponds, and lakes. Algae contain chlorophyll and are capable of growing through photosynthesis, a process that uses sunlight to convert carbon dioxide and other nutrients into organic compounds for growth.

Two types of organisms can occur in these places—true algae and cyanobacteria. Algal cells are larger than cyanobacteria and contain chloroplasts, a defined structure within algae where chlorophyll is stored. The cyanobacteria are sometimes referred to as blue-green algae and have a different cell structure than true algae. Algae are plant-like organisms (Fig. 17.9), and blue-green algae are bacteria.

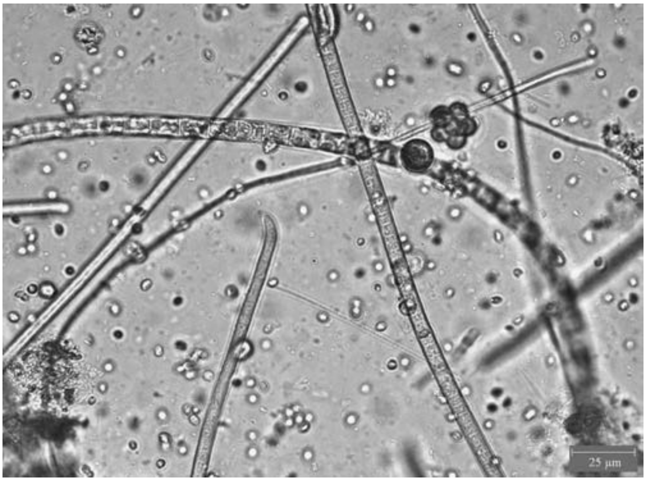


Figure 17.9 Photomicrograph of algal cells showing the complex cell clusters and long, plant-like strings of cells joined together (40×).

Cyanobacteria also use chlorophyll and light to convert carbon dioxide and water to oxygen and complex organic molecules.

The primary problem caused by algae is the plugging of distribution decks on cooling towers, resulting in loss of efficiency of the cooling tower. Chunks of algae can break loose from the top deck and cause exchanger pluggage or fouling. The dense, fibrous mats of algae can also provide areas for subsequent growth of anaerobic bacteria under the algae deposits. Living or dead algae can also act as a food source for the slime-forming bacteria that can flourish in this environment.

Protozoa

Protozoa are single-cell organisms that have mobility and feed by ingesting particulate materials such as bacteria. There are four types of protozoa found in nature, with the amoeba being the most commonly observed in cooling water systems. Protozoa in cooling water systems are an indicator of serious microbial contamination. Protozoa often exist in an environment that contains a large and diverse bacterial population along with organic nutrients, on which the protozoa can feed. When protozoa are present, the bacterial population is generally out of control. Additionally, the presence of protozoa is of concern for *Legionella* control, since *Legionella* are known to use protozoa as hosts in order to survive (Chap. 20).

Fungi

Yeasts and molds are common fungi sometimes found in cooling water systems. Yeasts and molds grow in water-wetted areas, rather than on submerged surfaces. Growths of these organisms produce hard, rubbery slime on surfaces. Fungi grow on wooden structures, such as cooling tower fill and supporting members, and sometimes under bacterial or algal masses. Fungi generally attack the cellulose that provides the structural strength of wood. Fungal attack has different characteristics than chemical attack. Chemical attack most often causes delignification, whereas fungal attack can cause delignification, loss of cellulose, or both. Lignin is the binding material between the cellulose fibers in wood. Degradation of wood by chemical causes is covered in Chap. 16 (Cooling System Corrosion). The result of either fungal or chemical attack of wood is usually permanent loss of strength of the wood structure. The major characteristics of cooling tower lumber deterioration are shown in Fig. 17.10.

Fungi can cause either surface rot or deep, internal rot of wood. Organisms responsible for surface rot include members of the Ascomycetes class and Fungi Imperfecti. Ascomycetes are the fungi also responsible for the Dutch elm disease that devastated the elm tree population in the United States, Canada, and Europe. In cooling water systems, surface attack or soft rot occurs only in water washed or flooded portions of the cooling tower.

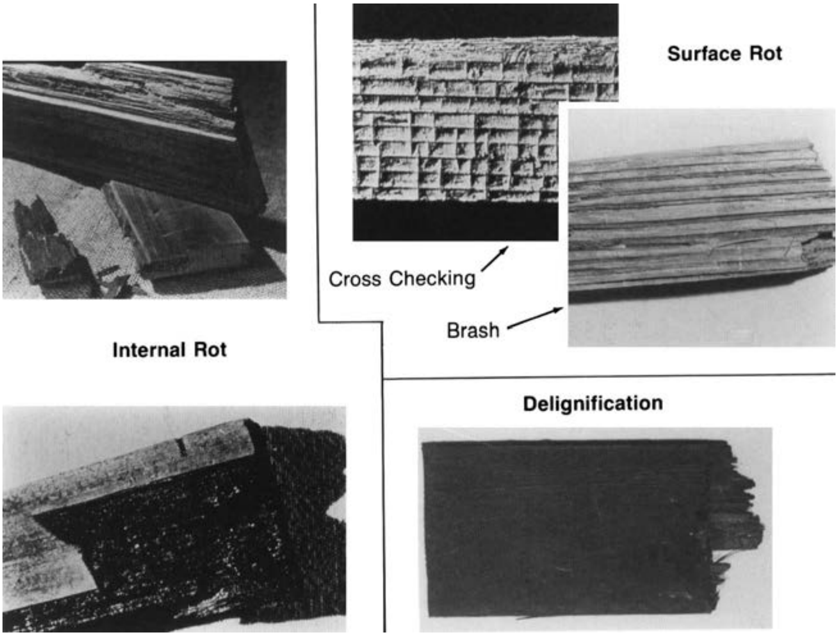


Figure 17.10 Typical examples of chemical or biological wood deterioration.

Fungi that produce deep or internal rot are members of the class Basiodiomycetes. These organisms consume wood components, such as cellulose and lignin, and are associated with brown rot, white rot, white pocket rot, and cubicle rot. In the Basiodiomycetes class, species of the genus *Lenzites* and *Poria* are commonly identified in samples of deteriorated wood.

The active growth of the wood-destroying fungi is confined to the surface layers and remains superficial, unless the wood is allowed to dry out frequently.

Factors Affecting Microbial Growth

An important factor affecting microbial growth is the degree of microbial contamination being introduced into a system. Another important factor is the amount of degradable material, or food sources, that are introduced to the tower. Microbes and their food can come from a variety of sources:

- Makeup water
- Airborne contamination
- Process leaks

- Organic debris
- Animal wastes
- Inadequate clean-up
- Inadequate dose of biocides (especially nonoxidizing biocides).

Controlling the source of microbial or organic contamination may not be possible depending on the source. For example, windblown dust that carries bacteria into a tower can be difficult to prevent. Controlling other factors of growth, such as the essential elements for growth or conditions suitable for growth, may also be difficult.

Suitable Conditions

Oxygen

Aerobic bacteria require oxygen and are found in aerated waters such as in a cooling water system. The main source of energy for aerobic bacteria is the oxidation of organic substances, with molecular oxygen as the electron acceptor. Anaerobic bacteria do not use oxygen and obtain energy from reactions of other substances or ions in solution. The reduction of sulfate to the sulfide ion and oxidation of ferrous ion to ferric ion are examples. Since anaerobes do not need molecular oxygen, anaerobic bacteria are found in oxygen-deficient areas, such as under deposits, in crevices, and in sludge.

Solution pH

Microbes have been found to exist in the broad pH range of 1 to 13. However, the most common microbes associated with water, algae and bacteria, prefer a neutral aquatic environment. Generally, yeasts and molds favor lower pH, in the range of 3 to 4. Bacteria and fungi can both contribute to industrial problems over a pH range of 3 to 10.

Temperature

Many species of microbes living in soil and water thrive in a rather broad temperature range of 50 to 125°F (10–52°C). Nature has produced a few organisms that can live at temperatures as low as 32°F (0°C) and as high as 212°F (100°C) (Fig. 17.11). Higher temperatures generally kill all common microbes, but scientists report finding life in hot springs and adjacent to ocean vents on the sea floor at temperatures of over 390°F (200°C). Therefore, most cooling water systems are within the ideal temperature range for microbial growth.

Sunlight

Organisms containing chlorophyll are able to use the radiant energy of the sun or artificial lighting to convert CO_2 to carbohydrates, which is needed for cell synthesis. However, not all radiant energy is useful

Figure 17.11 Thermophilic algae and bacteria growing in the outflow from one of the hot springs at Yellowstone National Park. (*NPS Photograph Courtesy of the National Park Service.*)

to the cell and certain frequencies of radiation are harmful. Ultraviolet radiation is an example of one method of microbe control.

Biofilms

Biofilms are encountered in a variety of everyday environments. Plaque on teeth and slime found in a household drain are both examples of biofilms. Biofilms are the result of bacteria and other microbes that adhere to surfaces and produce a mixed population. Some bacteria produce an extracellular, glue-like substance (polysaccharide) to which a variety of particles can adhere.

In cooling water systems, microbes exist both in the flowing water (planktonic organisms) and attached to surfaces (sessile organisms) (Fig. 17.12). The vast majority of the microbes in a cooling water system are sessile and live in biofilms. The biofilms may contain particulate organic matter, mineral scale, corrosion products, sediment, and other microorganisms (protozoa, fungi, and algae). The contaminant sources can be the surrounding air, the source water, or process leaks.

Formation and Growth

In cooling water systems, planktonic bacterial cells are routinely monitored. This method has proven to be a useful assessment of the microbial levels, despite the fact that a small minority of microorganisms in a cooling water system is planktonic. The sessile cells are the more prevalent microorganisms that are attached to the surfaces in the form of biofilms. Figure 17.13 shows a schematic representation of the stages of biofilm formation. Initially, planktonic cells are

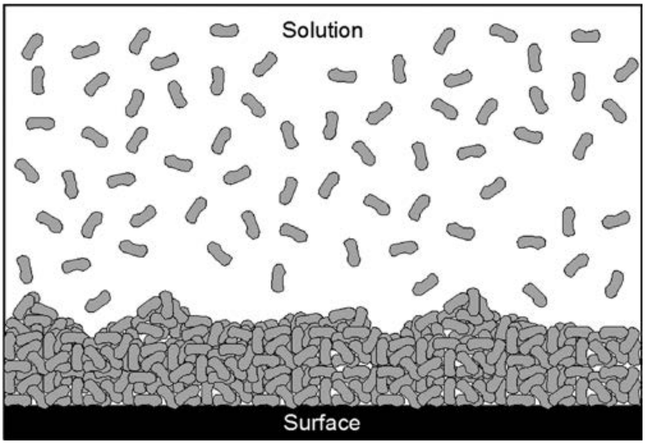


Figure 17.12 Biofilm on a surface may have 10 to 100 times as many sessile bacteria compared to the amount of planktonic bacteria floating in the water.

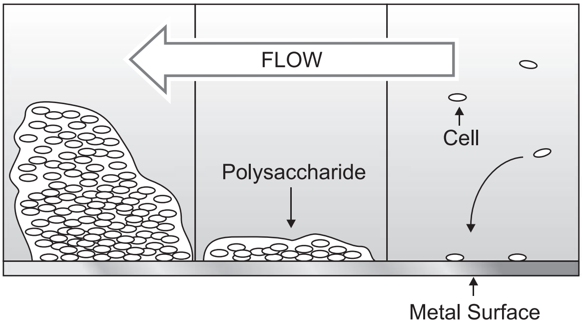


Figure 17.13 Stages of biofilm formation.

attracted to the surface, and weak bonds form between the bacterium and the surface. This may simply be an electrostatic attraction, which will depend on the type of microorganism, the type of surface, and a variety of conditions, such as pH and temperature. Once bonded to the surface, the microorganism changes. One visible change is that the sessile cells begin to secrete protein and polysaccharide slime. Cells turn on the gene responsible for synthesis of this slime after the cell is attached to the surface.

The bacteria in biofilms are able to grow, multiply, and attract other bacterial species as a complex community develops. Biofilms are dynamic in nature, with biomass sloughing off and being replaced by growth and attraction of other planktonic microorganisms. The rate of growth of a biofilm can be extremely fast, completely covering a surface in a matter of days.

Biofilm Advantages to the Microbes

Growth in biofilm provides several advantages to microbes. The biofilm provides a diverse consortium of organisms, increased availability of nutrients, and protection from antimicrobial agents. In a mixed, diverse population of microorganisms, exchange of metabolites can occur so the microorganisms can work together, each for their own benefit. The nature of the biofilm, especially the extracellular polymeric material, is believed to have the ability to attract and hold nutrients and ions that the bacteria in the biofilm need for growth.

Sessile cells are better protected from the environment than are free planktonic cells. Sessile bacteria are much more difficult to control with biocides than are planktonic bacteria. There are a few possible explanations for this phenomenon. The biofilm may prevent penetration of antimicrobial agents into the depths of the film. The concentration of antimicrobials in fluid beneath the biofilm surface would then be reduced. A likely reason for restricted penetration is that antimicrobials react with outer layers of the biofilm so the biocide is consumed before the biocide can penetrate into the film. Penetration rates are slower than the rate of reaction with the surface of the biofilm.

A further explanation is that a resistant microorganism may develop inside the biofilm. If nutrients are scarce, some microorganisms “shut down” or enter a waiting state, while other microbes may form spores. These would be resistant to kill by antimicrobials. Even in nutrient rich environments, attached microorganisms may have the ability to form resistant cells. All of these explanations for biofilm resistance to antimicrobial agents are the subject of ongoing research.

Problems Associated with Biofilms

Biofilms are responsible for reduced heat transfer efficiency in heat exchangers, reduced cooling tower efficiency, reduced flow, and increased under-deposit corrosion in cooling water systems. Biofilm can reduce heat transfer efficiency to a greater extent than other foulants on tube surfaces. Biofilms are at least four to five times more insulating than mineral scale deposit of comparable thickness (Refer to Fig. 17.2, shown earlier). In cooling towers, pluggage of the distribution deck can reduce flow and evaporation in the tower. Biofilm can contain corrosion products, mineral scale, and sediment in addition to microorganisms. Biofilms growing on parts of the tower can slough off surfaces and plug heat exchanger tubes (Fig. 17.14).

The ability of biofilms to reduce flow in pipes is well documented. Fluid flowing through a pipe experiences drag from interaction with

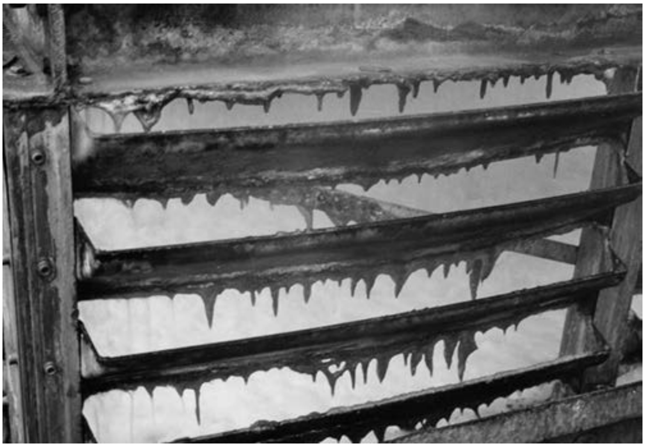


Figure 17.14 Example of biofilm hanging on water-wetted louvers near the basin of a cooling tower. The biofilm may contain bacteria, fungi, and inorganic material. If the biofilm falls off the louvers, plugging of heat exchanger tubes can occur.

the pipe surface. This drag reduces the flow velocity and requires an increase in pressure to maintain a given flow rate. Biofilms have been shown to reduce flow by over 50% in large diameter piping. Most of the losses have been associated with increase in surface roughness creating greater fluid frictional factors. In some contaminated systems, biofilms can be formed as floc particles that move with fluid flow and can be considered as "fluidized" biofilms.

Corrosion due to biofilms can be as serious as the lost heat transfer efficiency. Microbial biofilms can cause concentration cell corrosion that occurs under deposits. Biofilms are responsible for microbiologically influenced corrosion (MIC). MIC is corrosion either directly induced or indirectly influenced by microbes and biofilms. SRB can affect corrosion by the metabolic production of sulfide ions (S^{-2}). Acid producing bacteria have already been mentioned as a source of corrosion in cooling water systems. These microorganisms and the acids they produce are responsible for the low pH microenvironments that can be observed under biofilms. Additionally, depletion of oxygen in the layers of biofilm in contact with the metal surface can lead to anaerobic conditions, setting up a condition referred to as a differential oxygen cell. All of these conditions create an environment where corrosion is enhanced. Under-deposit corrosion, concentration cell corrosion, differential oxygen cell corrosion, and MIC are all discussed more fully in Chap. 16 (Cooling System Corrosion).

Determining the Bacterial Population of Cooling Water

The differential microbial analysis (DMA) is a set of laboratory tests, which offers a profile of many microorganisms found in cooling water systems. DMA testing is not performed as frequently as on-site testing (like dip-slides described in Chap. 18) but periodic DMA testing can be an important part of an effectively managed microbial control program. It should be done periodically, with the frequency dependent on the level of microbial problems.

DMA provides important information about the microbiology of the cooling system. It can differentiate the bacteria in Table 17.1 (earlier in this chapter) by growing them on agar plates. Figure 17.15 shows a typical agar plate with mucoid and pigmented bacterial colonies grown from a cooling water sample. Other organisms, like algae, protozoa, and fungi can be determined by microscopic observation. Figure 17.16 shows an example of a DMA report with a typical distribution of organisms found in an open recirculating cooling water system. In this water sample, a variety of typical aerobic bacteria are present, a very small amount of anaerobic bacteria may be present, yeasts and molds are very low, and no other troublesome organisms are found.

The DMA monitors planktonic bacteria, those floating in the water, or sessile bacteria, which are those on surfaces. Planktonic bacteria are measured in water samples while sessile bacteria are

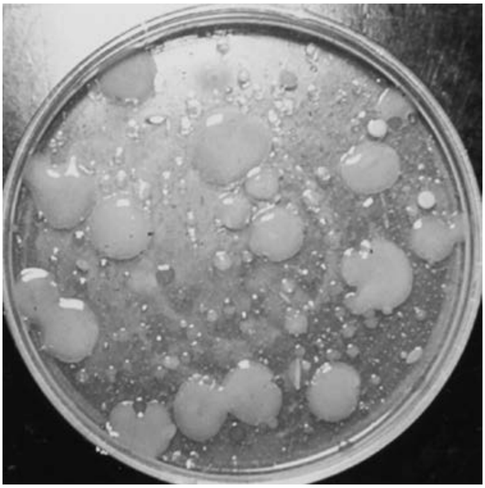
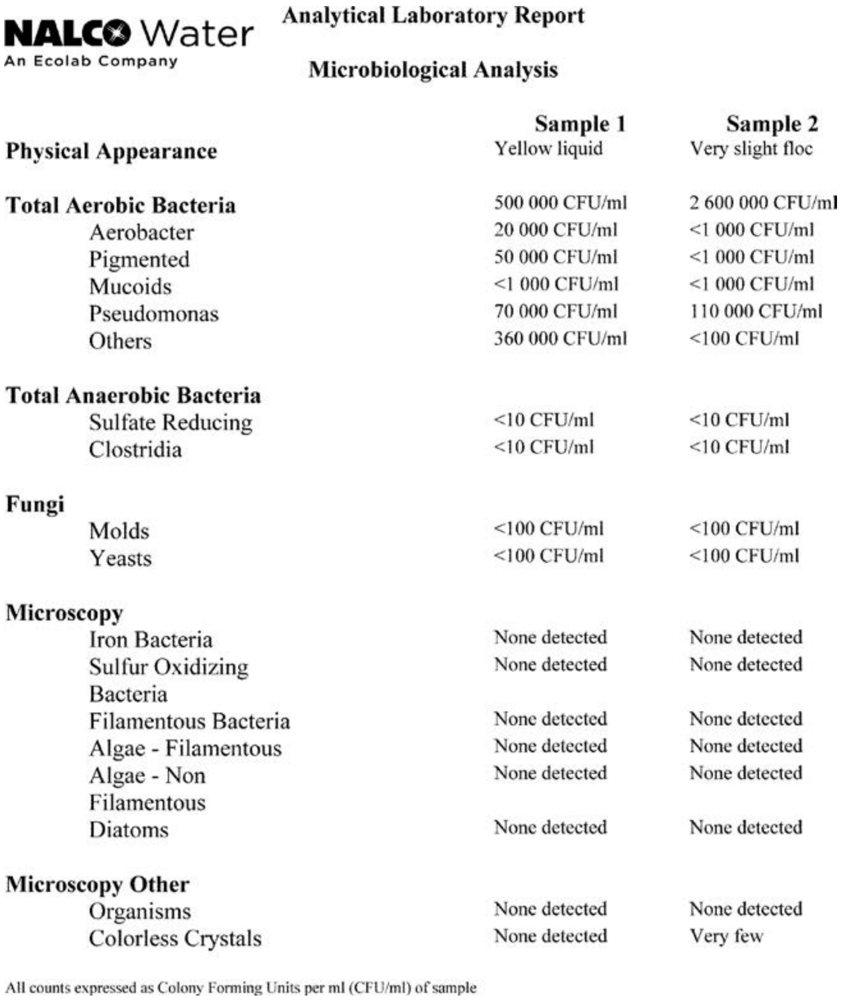


Figure 17.15 Example of bacterial cell cultures from cooling water system grown on an agar plate as part of a DMA.



NALCO Water
An Ecolab Company

Analytical Laboratory Report

Microbiological Analysis

	Sample 1	Sample 2
Physical Appearance	Yellow liquid	Very slight floc
Total Aerobic Bacteria	500 000 CFU/ml	2 600 000 CFU/ml
Aerobacter	20 000 CFU/ml	<1 000 CFU/ml
Pigmented	50 000 CFU/ml	<1 000 CFU/ml
Mucoids	<1 000 CFU/ml	<1 000 CFU/ml
Pseudomonas	70 000 CFU/ml	110 000 CFU/ml
Others	360 000 CFU/ml	<100 CFU/ml
Total Anaerobic Bacteria		
Sulfate Reducing	<10 CFU/ml	<10 CFU/ml
Clostridia	<10 CFU/ml	<10 CFU/ml
Fungi		
Molds	<100 CFU/ml	<100 CFU/ml
Yeasts	<100 CFU/ml	<100 CFU/ml
Microscopy		
Iron Bacteria	None detected	None detected
Sulfur Oxidizing Bacteria	None detected	None detected
Filamentous Bacteria	None detected	None detected
Algae - Filamentous	None detected	None detected
Algae - Non Filamentous	None detected	None detected
Diatoms	None detected	None detected
Microscopy Other		
Organisms	None detected	None detected
Colorless Crystals	None detected	Very few

All counts expressed as Colony Forming Units per ml (CFU/ml) of sample

Figure 17.16 Typical DMA report from an open recirculating cooling water system under reasonably good control.

measured in samples swabbed from a surface in the cooling water system. It is the sessile bacteria on the exchanger surfaces that affect the heat transfer efficiency of the system and can cause under-deposit corrosion. A very high proportion of the bacteria in cooling systems live on system surfaces. Monitoring the planktonic bacteria can give an indication of the bacterial population of a system, but there is no correlation between planktonic counts and the amount of sessile bacteria on surfaces of a system. Therefore, control of microbial growth is essential for optimum results in cooling systems.

CHAPTER 18

Cooling Water Monitoring

Monitoring of cooling systems is critical to ensure optimum performance and to maximize efficiency. Generally, monitoring can be divided into methods to evaluate performance and system control. Performance evaluation includes methods to determine the amount of deposition, corrosion rates, and microbial growth and fouling. Methods to evaluate system control generally involve analysis of water samples.

Deposition Monitoring

Many different deposit monitors are used in cooling systems, ranging from a simple mesh screen to entrap deposits to small shell-and-tube heat exchangers that must be opened to observe deposition. The most common types involve a heated tube to simulate a heat exchange surface. Specialized biofouling monitors range from boxes containing removable test surfaces that entrap microbial organisms to pressure drop monitors that measure change in pressure across a smooth tube as microbial fouling occurs. Online deposit monitors, based on a piezoelectric crystal, have been developed that measure the rate of deposition on the crystal surface.

Removable sections of tower fill and strain gauges are often used to monitor fill fouling in cooling towers. New nonintrusive technology to map tower fill density and location is also used.

Heated Tube Deposit Monitors

These monitors have an internally heated tube, so that the surface exposed to water can be observed as deposition occurs. The more accurately the monitor simulates conditions of the heat exchanger in question, the more closely deposition simulates results in the exchanger. Even so, the deposit monitor is only a simulation of conditions in an exchanger. Thus, results must be interpreted with care and correlated to actual exchanger performance and inspections.

FIGURE 18.1 Example DATS® deposit monitor. (*Courtesy of Bridger Scientific*.)

Tube-based deposit monitors are available in a variety of styles. A typical deposit monitor allows for continuous on-site monitoring of deposition on a heat transfer surface in a cooling water system. Metallurgy of the sample tube, water flow rate, heat flux, and skin temperature can be selected to simulate conditions of a specific heat exchanger. Tube skin temperature can be monitored to allow calculation of heat transfer coefficient (U value) or fouling factor of the deposit monitor tube. Trends of fouling rate can be obtained to relate to program performance in the plant. Another commercially available unit is the Deposit Accumulation Testing System (DATS® made by Bridger Scientific, Inc.) as shown in Fig. 18.1. There are several different configurations of this unit. The DATS monitor operates in a similar manner to the tube-based monitor.

Pressure Drop Microbial Fouling Monitors

An example of this type of deposit monitor is shown in Fig. 18.2. Typically, a specially designed tube with a differential pressure gauge is used to measure pressure drop across the tube. As biofilm develops, pressure drop increases; as biocontrol is regained, pressure drop correspondingly decreases. Biofilms as thin as 1 mil (25 µm) can usually be detected.

Real-Time Deposit Monitoring

A piezoelectric quartz crystal microbalance can monitor changes in fouling over short time periods and is sometimes called a real-time monitoring device (Fig. 18.3). The crystal vibrates when current is applied, and vibration frequency changes in proportion to the mass of deposition on the crystal surface. Changes in deposition can be

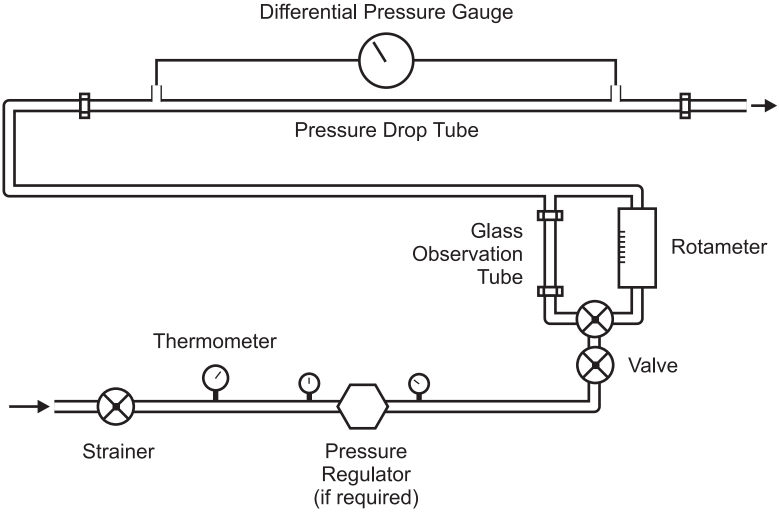


Figure 18.2 Typical biofouling monitor using a pressure drop tube.

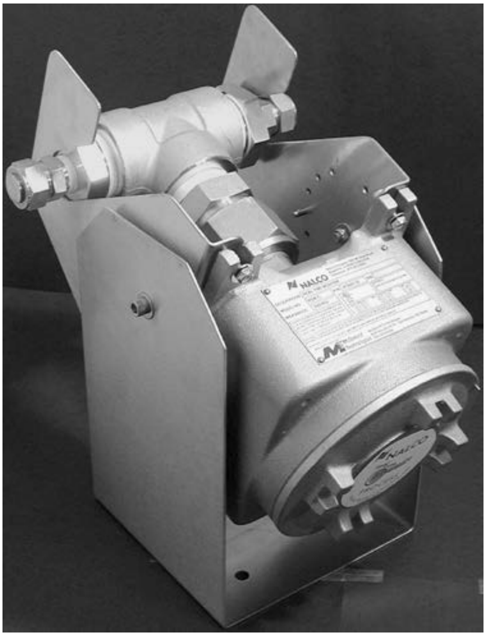


Figure 18.3 Example of a real-time deposit monitor.

measured rapidly, and by monitoring changes in the signal over time, trends of fouling from both mineral scale and soft deposits like microbial slime can be obtained. The crystal surface may not be heated, and the surface may have different characteristics from a heat transfer surface. These monitors are generally used for shorter periods than tube-style deposit monitors. They are most useful for showing the effect of changing conditions or programs rather than simulating an actual exchanger fouling rate.

Corrosion Monitoring

The purpose of corrosion monitoring is to assess or predict corrosion behavior of a system. Corrosion monitoring is standard practice in the water treatment industry and has several uses:

- To make a rough prediction of equipment life
- As a diagnostic tool to help solve corrosion problems
- Show effectiveness of treatment programs or effect of changes to operating parameters
- Correlate corrosion trends to control parameters

The particular corrosion monitoring technique selected depends upon its applicability to the system and information desired. Most corrosion monitoring techniques are best suited to situations where corrosion is of a general nature, but some techniques provide information on localized attack such as pitting. Specific examples are given in Table 18.1, with description of what is measured and application of each monitoring technique. More than one method may be necessary to properly evaluate efficacy of a treatment program in a system. Each technique has specific characteristics that lend themselves to different applications.

Corrosion Coupons

The simplest corrosion monitoring technique is to place a metal coupon (small strip of metal) in flowing cooling water for a given time. Coupons are made from many alloys, and appropriate alloys should be selected to match metals in the system.

Coupons must be placed in a coupon test rack for best comparison to system results, and for best consistency from one exposure period to another. Data gathered have value only if coupons are properly installed. A typical installation of coupon and holder for cooling systems is shown in Figs. 18.4 to 18.6. Coupons should be placed where conditions simulate the environment being evaluated. For example, if the objective is to evaluate corrosion potential in a critical exchanger, a coupon rack should be installed at the outlet of this exchanger, so that water temperature is representative of

Method	Measures	Applications
Corrosion coupons (small, metal specimens)	Average corrosion rate is determined by mass change of coupon over a period of typically 30–90 days. Can be used for pit depth measurements.	Best for uniform corrosion under steady-state conditions. Can show localized attack by pitting and under-deposit corrosion. Coupons are available for most alloys.
Linear polarization resistance (LPR) (e.g., Nalco NCM100 and Corrater)	Instantaneous corrosion rate is measured by electrochemical polarization between two electrodes. Tendency for pitting (pitting index) can be measured.	Water must have sufficient conductivity to provide suitable measurement of corrosion rate. Suitable for common engineering alloys.
Electrical resistance (ER) (e.g., Corrosometer)	Corrosion rate is determined by electrical resistance change from thickness loss of a corroding metal wire. Uniform corrosion rate is assumed in calculation.	Works in zero to high conductivity environments, either liquid or vapor using most alloys. Gives general corrosion rate even if localized corrosion is occurring.
Analytical monitoring	Concentration of dissolved or suspended species in water, such as corrosion products, pH, and conductivity. Does not measure corrosion rate directly.	Trends of dissolved or suspended corrosion products may be proportional to changes in corrosion rate. Precipitation of these corrosion products limits technique effectiveness.
Deposit monitors [e.g., Deposit Accumulation Testing System (DATS)]	Visual observation of corrosion on heat transfer surface. Metal tube can give average corrosion rate from mass loss data and pit depth measurements.	Suitable in simulating conditions of heat exchanger, if alloy is the same as in the exchanger and water temperature and heat flux are similar. Heat transfer tubes can be made from most alloys.

Corrater® and Corrosometer® are Trademarks of Rohrback Cosasco Systems; DATS® is a Trademark of Bridger Scientific, Inc.

Table 18.1 Examples of Monitoring Techniques with Parameters Measured and Applications

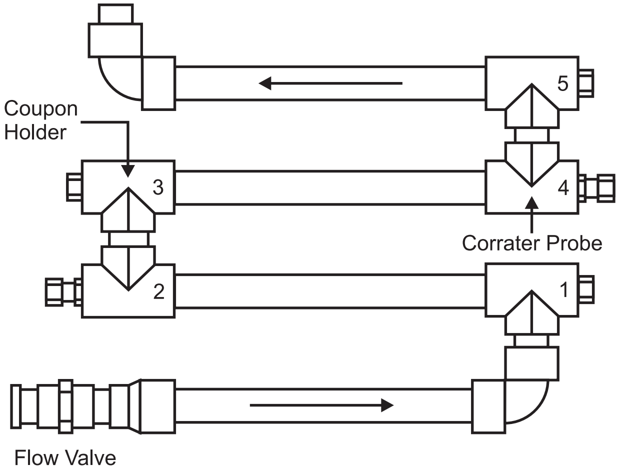


Figure 18.4 Illustration of a corrosion test rack.

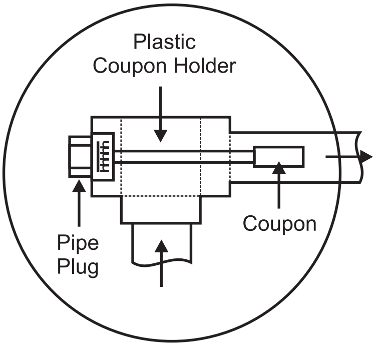


Figure 18.5 Illustration of a correct corrosion coupon installation in the rack.

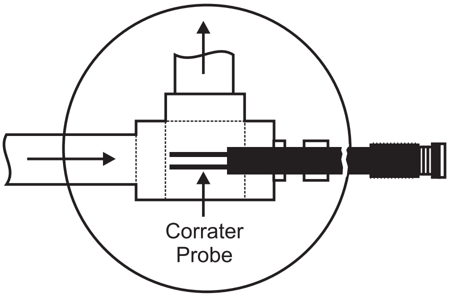


Figure 18.6 Illustration of a correct LPR probe installation in the rack.

that exchanger. Deposit monitor tubes are also used to approximate heat exchanger corrosion rates, since tubes are heated to similar skin temperatures.

Coupon Exposure

Typically, coupons are exposed to system water for 30 to 90 (90 preferred) days. This exposure period is needed, particularly for mild steel, to avoid abnormally high corrosion results from initial corrosion effects during the first few days of installation. Initial corrosion rates on steel coupons can be very high, because the bare metal surface is in an active state due to lack of a protective oxide layer. Figure 18.7 shows decrease in corrosion rate with exposure time for mild steel. Steady state is normally achieved in several days to a week, depending on conditions. A common approach is to use three sets of coupons, placed in a test rack and changed in sequence of 30-, 60-, and 90-day intervals. Normally, with longer exposure period, coupons more closely approximate conditions in the system.

It is common to install several corrosion coupons of the same type, so that one can be removed for analysis each month (after the appropriate 90 days). In this way, monthly corrosion data can be reported.

Occasionally, such as during a program transition, it is desired to obtain data after as short as one month after transition. This can be done; however, there should be a one-month exposure coupon taken just prior to the conversion, as a comparison. As stated, exposure of that short a period will show abnormally high corrosion rates, compared to coupons exposed for 90 days. This way timely results can be seen, but also compared to the previous conditions. Typical 90-day results would then be used for final determination of transition success.

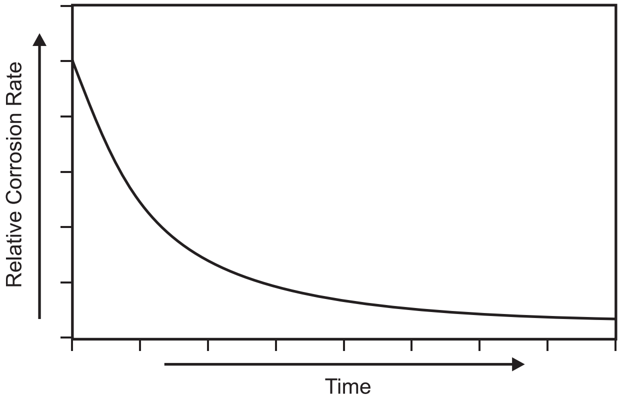


Figure 18.7 Coupon corrosion rate is very high when first installed in cooling water, decreasing to steady state after a few days to a week.

Coupon Evaluation

After coupons are removed from the system, they should be evaluated by a metallurgical analytical lab. This involves cleaning the coupon in a specialized manner, determining the new mass of the coupon, and calculating the corrosion rate based on mass loss. The corrosion rate is reported in mils per year (mpy) or micrometers per year (μm/y), along with a description of the type of corrosion attack. Common standards for description of the type of corrosion are:

- General corrosion—uniform corrosion over entire surface
- Localized attack—isolated areas of corrosion
- Pitting—small, deep, isolated areas of corrosion where depth of penetration exceeds width of pit mouth

Examples of these are shown in Fig. 18.8. When pitting or localized corrosion occur, the general corrosion rate can grossly underestimate severity of a corrosion problem. In this case, type and depth of attack should be noted.

Actual pit depth can be measured using a specially designed pit depth microscope, schematically shown in Fig. 18.9. This direct

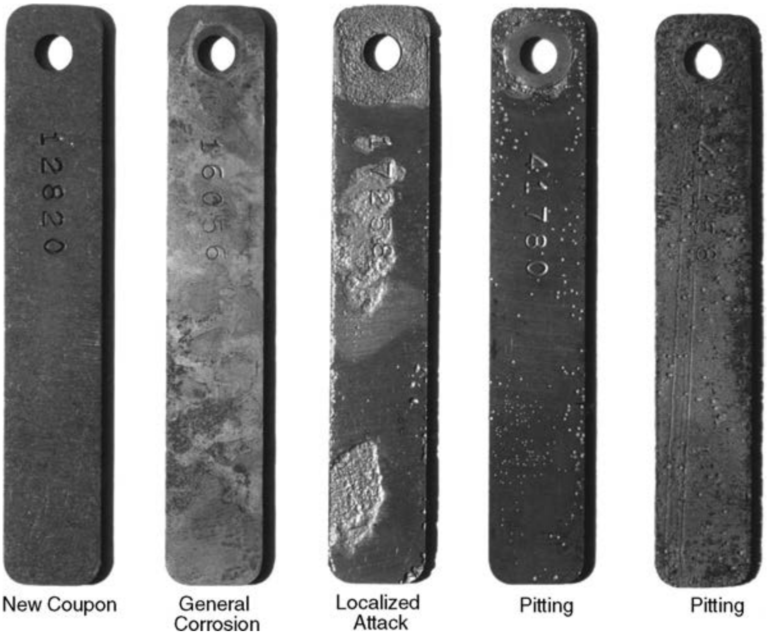


Figure 18.8 Examples of corrosion that fit standard descriptions of types of corrosion on a mild steel coupon.

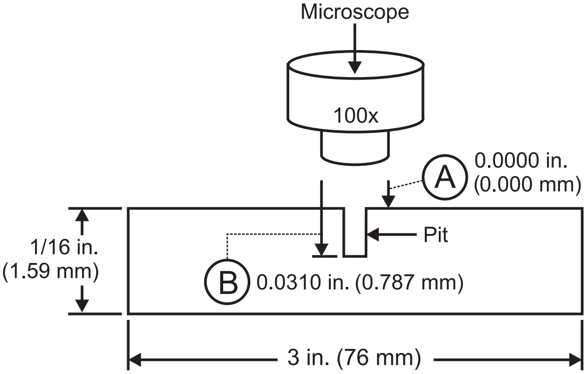


Figure 18.9 Measurement of pit depth by difference between coupon surface and bottom of pit.

measurement determines actual penetration of metal during exposure of the coupon. Typical microscopes can measure pit depth to a resolution of 0.1 mil (2.5 μm). The coupon report of corrosion rate should include this pit depth measurement, in addition to an average corrosion rate.

Typical Range of Corrosion Rates

The desired goal for corrosion rates should be determined individually for each given system. Typical classifications for corrosion rate values are shown in Table 18.2. Note that these are typical definitions or descriptions of different ranges of corrosion coupon results. Individual system operators may have tighter requirements

Corrosion Rate, mpy (μm/y)		
Mild Steel Coupons	**Copper Alloys**	**Description of Results**
<1 (<25)	<0.1 (<2.5)	Excellent (negligible corrosion)
1–3 (25–76)	0.1–0.25 (2.5–6.4)	Very good (minimal corrosion)
3–5 (76–127)	0.25–0.35 (6.4–8.9)	Good (moderate corrosion)
5–8 (127–203)	0.35–0.5 (8.9–12.7)	Poor (moderately high corrosion)
8–10 (203–254)	0.5–1.0 (12.7–25)	Bad (high corrosion)
>10 (>254)	>1.0 (>25)	Unacceptable (severe corrosion)

Table 18.2 Generally Accepted Ranges for Corrosion Performance

for corrosion performance, depending on criticality of the process involved.

Electrochemical Corrosion Monitoring

The two most common electrochemical techniques for online, real-time corrosion monitoring are linear polarization resistance (LPR) and electrical resistance (ER). Table 18.1, shown earlier, provides some characteristics of these two methods. Corrosion rate trend data generated by these methods are more valuable than any single reading taken alone. Changes in trend data can be very valuable for troubleshooting.

Linear Polarization Resistance

Corrosion occurs due to electrochemical corrosion reactions. The rate of corrosion is proportional to current flow in the electrochemical cell. Current flow is dependent on resistance of the solution (solution resistance) and resistance caused by any inhibitor film on the metal surface (polarization resistance). In typical conductivity of cooling water, solution resistance is negligible. Therefore, the corrosion rate can be determined with LPR based on polarization resistance alone. The LPR technique measures instantaneous corrosion rate, since a complete scan takes less than a minute.

LPR monitors can provide corrosion rate data within a few hours to several days after installation. Depending on metal used, probe tips need some time for passivation by treatment in the system. This instrument is well suited to applications where upsets or other accelerated corrosive conditions must be detected quickly, so that remedial action can be taken. The corrosion rate obtained with LPR techniques assumes uniform corrosion, but some instruments can show pitting tendency (pitting index).

LPR can be inaccurate in low conductivity waters such as once through cooling water, soft cooling water, and boiler condensate, because the magnitude of solution resistance can be significant. (Remember, LPR measures the sum of solution and polarization resistance as the corrosion rate.) Two commercially available devices that use LPR are the Corrater made by Rohrback Cosasco Systems and the Nalco NCM100. The NCM100 (Fig. 18.10) and some models of the Corrater have compensation for low conductivity solutions, and can be accurate in water with conductivity as low as 10 μS/cm.

Electrical Resistance

Conventional electrical resistance (ER) probes for corrosion rate measurements consist of a metal wire element embedded in a water-resistant material. As corrosion proceeds, cross-sectional area of the metal wire decreases, causing an increase in ER of the wire. By measuring change in electrical resistance, the corrosion rate can be determined.

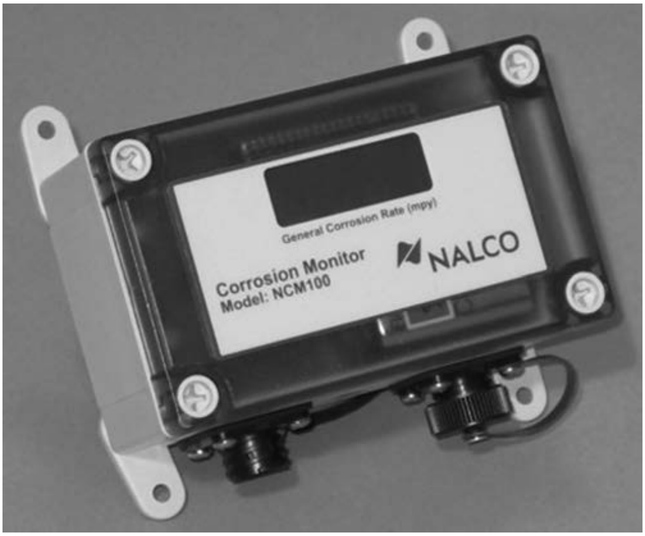


Figure 18.10 Example of an LPR-based instantaneous corrosion monitor.

This ER technique can be used for corrosion rate measurements in liquids or vapors. The liquid does not have to be conductive to obtain results. The disadvantage is that ER does not measure instantaneous corrosion rate. Usually, at least a week is required to obtain a significant change in electrical resistance, especially in well-treated cooling water systems. In addition, the ER method cannot detect localized corrosion such as pitting. The Corrosometer, manufactured by Rohrback Cosasco Systems, is an example of an ER corrosion monitor.

Corrosion Product Monitoring

Monitoring either iron concentration for steel components or copper concentration for copper-based alloys can be useful for evaluating corrosion trends. This method assumes that the concentration of ions in solution released by corrosion reactions is an indication of the severity of corrosion. This assumption is not always correct, because metal ion concentration in the sample can be affected by a variety of system conditions, such as:

- Iron in the makeup water directly influences iron concentration in the system.
- Iron deposits in the system or airborne contamination may release iron into water.
- Sample collection techniques can affect analytical results for sparingly soluble ions like iron.

- Accurate iron testing is required; the difference between 0.6 mg/L and 0.8 mg/L may be insignificant.
- Iron corrosion products tend to precipitate.

Even with these constraints, corrosion product ion analysis can still be valuable for monitoring trends in corrosion. To effectively use this technique, a procedure must be established and rigorously followed, so that analysis of results is of value. The procedure should include sampling protocol, sampling frequency, and using the same analytical method for all samples. Statistical process control (SPC) techniques should be used for analyzing variations in trends.

Biological Growth Monitoring

Monitoring biological growth and biofouling are essential for proper control and operation of cooling systems. A variety of techniques is available, including biofouling monitors described earlier in this chapter. Using several methods to monitor a system generally yields the best results.

Lab Methods

A common method to determine the quantity and type of organisms in a cooling system is to send a water sample to a special analytical laboratory for microbial analysis. Several methods including growing bacteria on agar plates, microscopic analysis, and wood analysis for fungi are available.

Plate Count Methods

The most common technique to estimate the number of living (viable) cells in a water sample is the plate count or colony count method. Small amounts of different dilutions of the water sample are applied to agar growth medium in Petri plates. After a suitable incubation time (usually two to three days), the number of colonies that have developed is estimated. The number of colony-forming units per milliliter (CFU/mL) is determined using the dilution factor for that plate. Many different growth media are available. One agar type is used to produce total aerobic colony count, while other types grow specific bacteria like slime forming, anaerobic-corrosive, or nitrifying bacteria.

This is the basis for the differential microbiological analysis (DMA) used in cooling water testing to gain an understanding of the types of microorganisms present. Total count is an indicator of relative contamination of a cooling system. Increase or decrease of total count by a factor of 10 or more signals significant change in the level of microbial contamination. However, total count understates the true bacterial population and does not measure bacteria in biofilm on surfaces. More detail on this method and an example DMA report is shown in Chap. 17.

Microscopic Examination

Two distinct types of microscopy are employed in examination of microbiological samples. The light microscope is used to see intact cells, while the electron microscope with its greater resolving power is used to study cell structure and details. The light microscope is valuable in classification of bacteria by various cell morphology, and the reaction of cells to various stains. Gram stain reagents are applied to microorganisms that have been fixed to a slide, and observation of the color of the cell is done with a microscope. Gram-positive bacteria appear purple, and gram-negative bacteria appear red. Figures 18.11 to 18.16 show a variety of different microbes that can be found in cooling systems.

Wood Samples

Wood in a cooling tower can be monitored periodically to prevent long-term fungal deterioration. Monitoring is usually conducted with wooden test specimens placed in the cooling tower. Test samples can be submerged, placed in constantly wetted areas exposed to air (fill section), or placed in areas with only moisture contact (plenum area). After a period, samples are analyzed in a laboratory for presence of fungi and their resistance to fungi growth. Results indicate if tower lumber is infected and what actions are required to minimize wood deterioration.

Field Methods

On-site testing is needed to provide more rapid information compared to sending a sample for detailed lab testing. Several methods exist, including a variation of the lab plate count method.

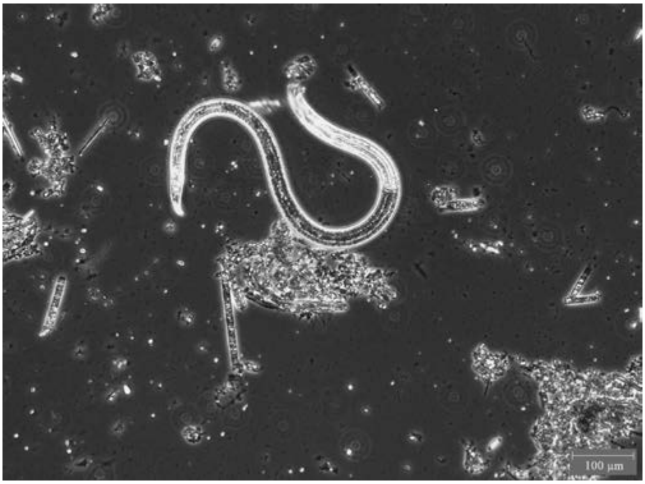


Figure 18.11 A photomicrograph of a Nematode.

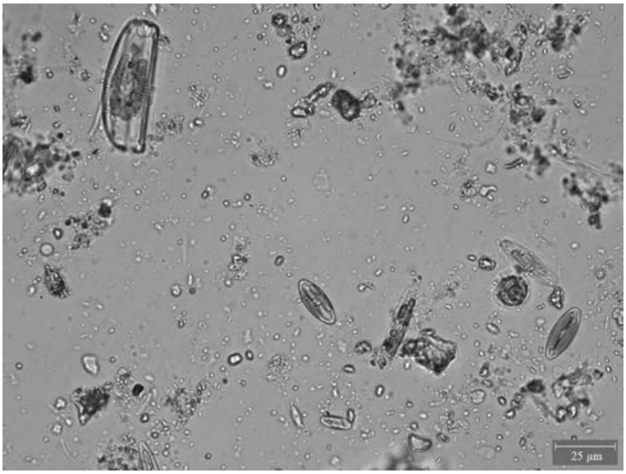


Figure 18.12 A photomicrograph of Diatoms.

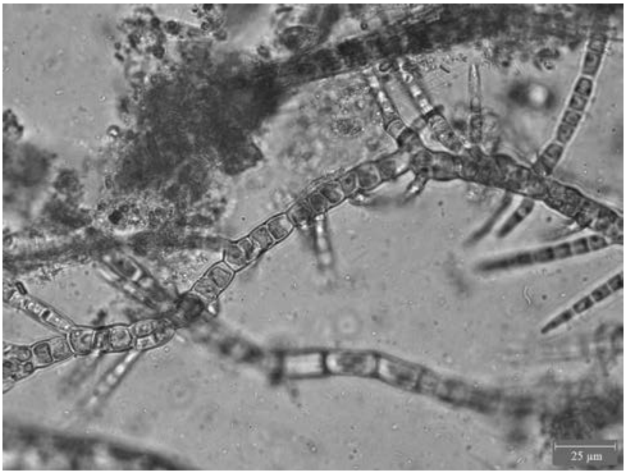


Figure 18.13 A photomicrograph of Filamentous algae.

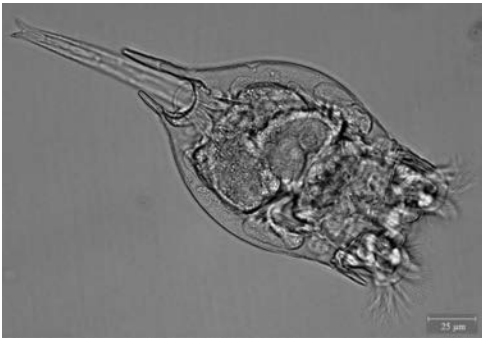


Figure 18.14 A photomicrograph of a Rotifer.

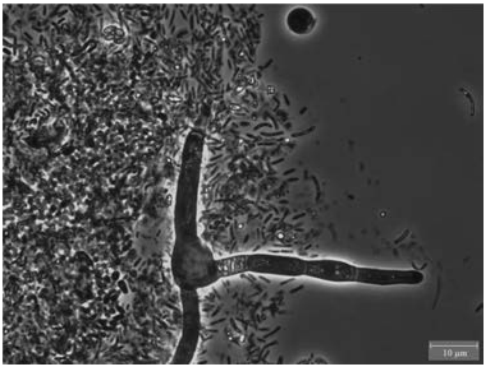


Figure 18.15 A photomicrograph of a fungal filament.

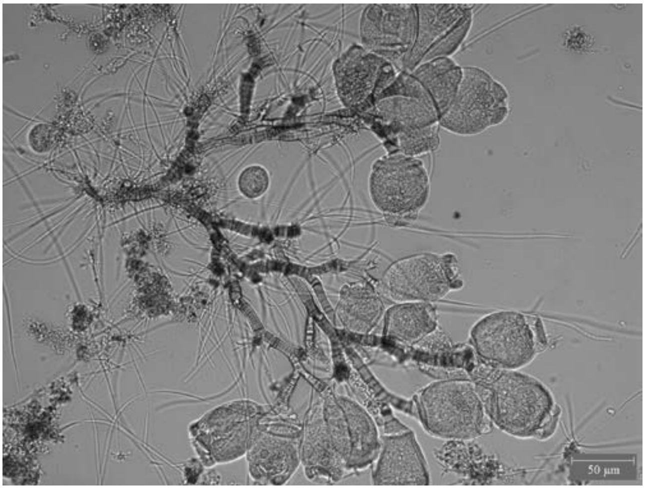


Figure 18.16 A photomicrograph of colonial stalked ciliates.

Dip Slides

The dip slide is a widely-used field test to monitor microbial activity in a system. This test is a simple version of the plate count method. Growth medium (dip slide) is immersed briefly in the water sample, and the slide is incubated in its container. A biologically active dye is present so that stained colonies are easily observed (Fig. 18.17). The slide is compared to a set of standard slides (Fig. 18.18) to estimate CFU/mL in the sample. Common dip slides provide an estimate of total aerobic bacteria and fungi as part of the same test. Other growth media are available to test for sulfate-reducing bacteria (SRB).

FIGURE 18.17 Microbes are collected and cultured by pretreated elements, which are easily incubated in the sampling container. (*Courtesy Millipore Corporation*.)

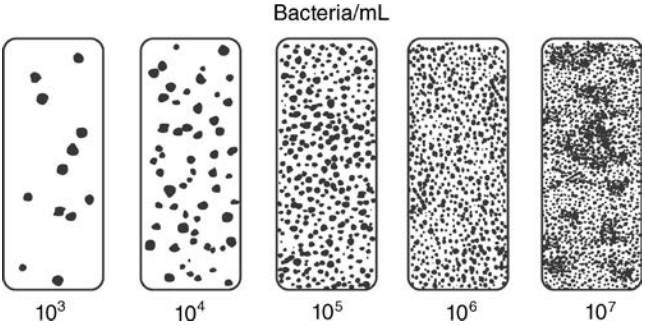


FIGURE 18.18 Chart for interpretation of dip slide results.

Dip slides are easy and quick to use, economical, and sensitive to a range of microbial levels. Results are available in two days, without need to send samples to a laboratory. However, they do not detect all types of microorganisms and cannot differentiate wide varieties of microorganisms.

Quick Dye Tests

Quick tests exist for rapid screening to estimate microbial growth in a water system. A water sample (usually 500 mL) is filtered through a fiberglass filter. Microorganisms collected on the filter pad are visualized with an indicator dye, which reacts with living microorganisms.

Intensity of the color is indicative of the number of colony-forming units present. The method is a rapid and inexpensive means to determine if high bacteria levels are present. The main disadvantage is that 10^5 CFU/mL must be present before a discernable color develops.

Adenosine Triphosphate

Adenosine triphosphate (ATP) is a critical chemical in the metabolism of all microorganisms. Therefore, measurement of ATP can be an indicator of the number of microorganisms present. In tests, microbial cells are disrupted to release ATP, which is then reacted with luciferin and luciferase to produce visible light. This is the common reaction used by the firefly to emit light. Intensity of light produced is measured using a photometer and related to the amount of bacteria present. Some ATP from dead organisms may be present in bulk water, and free ATP measurement (where cells are not disrupted) should be used as a blank. The ATP test is simple and can be quickly conducted in the field.

The main advantage of this method is a rapid assessment of the relative number of microorganisms present. The method is quite sensitive to low levels of biological activity, and it is widely used in the food and paper industries. The major disadvantages of the method are no absolute correlations to CFU/mL from dip slide or DMA results, no indication of the type of microorganisms present, and equipment and reagents are relatively expensive.

Having data on the amount of viable and free ATP in the system is very useful, as it indicates the presence, or previous presence, of many life forms that are not easily plated. Combined with plate counts for some microbes, the ATP measurement is a valuable tool.

Online Biological Monitoring

Several methods exist for online monitoring of biological control agents, particularly halogens. These can be used for controlling halogen dosage, but may result in overfeed if halogen demand fluctuates and becomes significant.

Halogen Monitors

Analyzers are available to monitor a sample stream for halogen content. These devices automate the diethyl-p-phenylenediamine (DPD) test to measure either free or total halogen up to 5 mg/L every few minutes. Control of halogen residual may be included within this working range. Devices are reliable and accurate but are more costly than other methods, and maintenance is required due to wet chemistry of the test method.

Oxidation Reduction Potential (ORP) Monitors

ORP is a convenient, cost-effective, and reliable means to monitor and control oxidant treatment in a system. Oxidants, like halogens,

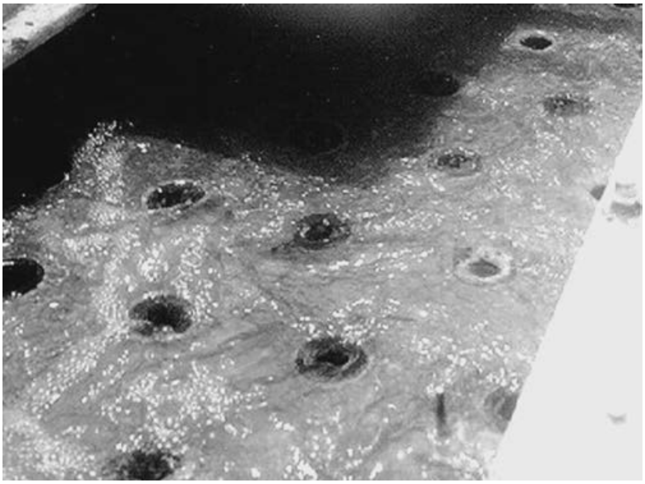


Figure 18.19 Open-deck cooling tower showing clean water distribution orifices and appropriate water level.

produce a potential difference (voltage) between a pair of electrodes that relates to concentration of oxidant in solution. The method is sensitive to halogen concentration within normal application range for biocontrol. Temperature and pH affect the potential reading, and some industrial ORP probes automatically compensate for temperature and pH changes. ORP can be used for control of all oxidizing biocides that produce measurable levels of halogen, including organic halogen release compounds but not stabilized halogens.

Many innovations in oxidant residual monitoring have been developed that include specific measurement of undissociated hypohalous acid, chlorine dioxide, ozone, and peroxides. Additional development has also occurred around probe maintenance that improves accuracy and reliability of measurement.

Visual Inspection

Direct observation of the cooling system is a valuable monitoring method. Look at sunlit areas of the cooling system for algae (Fig. 18.19), examine fill for slime, feel system surfaces for slime, and examine pipes and exchangers when access to them is available. A great deal can be learned from simple observation.

CHAPTER 19

Cooling Water Treatment and Control

Controlling deposition, corrosion, and microbial growth in cooling water systems is essential for optimizing system performance and efficiency. This chapter discusses methods to minimize deposition, corrosion, and microbial fouling in cooling systems. Chemical treatments and programs that combine both chemical treatment and control technology are covered.

Deposit Control Methods

A variety of control methods to minimize deposition are available. Water chemistry management can have a dramatic impact on scale control. Mechanical methods can affect both fouling and scale control. A wide variety of chemical inhibitors exists to improve control of scale and fouling. Most successful programs combine elements from each of these areas to improve overall plant efficiency.

Control of water chemistry and tower operation is a necessity. Examples of some areas to consider include:

- Alkalinity and pH control can minimize scale formation.
- Limiting concentration of critical ions can prevent scale formation and minimize corrosive ions like chloride and sulfate.
- Makeup water clarification or softening can reduce scale forming species or fouling materials.
- Sidestream treatment is an effective method of minimizing problems caused by suspended matter.
- Design factors that affect water velocity, flow patterns, water and surface temperatures, heat flux, or heat exchanger surface roughness can affect scaling and fouling.

- Practices to improve system cleanliness (air rumbling of exchangers or vacuuming tower basins) can help remove suspended solids.

These factors can be controlled or modified to improve results of any treatment program.

Deposit Inhibitor Mechanisms

Inhibitors for minimizing deposits include scale inhibitors, dispersants, and surfactants. Chemical scale inhibitors can work by a variety of means: threshold inhibition, crystal modification, sequestration (chelation), or dispersion. Dispersants work by keeping suspended particles in solution. Surfactants can help prevent or remove some types of deposits. A comprehensive program may use all three chemicals for minimizing deposits in a cooling water system.

Scale Inhibitor Mechanisms

The most common scale inhibitors work by three main mechanisms:

1. Threshold inhibition is a general term where substoichiometric amounts of inhibitor (i.e., much less than 1 mg/L of inhibitor per mg/L of scaling ion) retard precipitation.
2. Crystal modification disrupts orderly growth of scale crystals, causing them to be deformed and physically weak (Figs. 19.1–19.3.) Crystal modifiers can be adsorbed on crystal growth sites, slowing kinetics of crystal growth.
3. Sequestrants act like chelating agents by complexing scale forming ions into a soluble ion pair to prevent deposition. It is generally a less strongly formed bond than a true chelation complex. In cooling water, polyphosphates and anionic dispersants are sequestering agents for iron, manganese, and calcium.

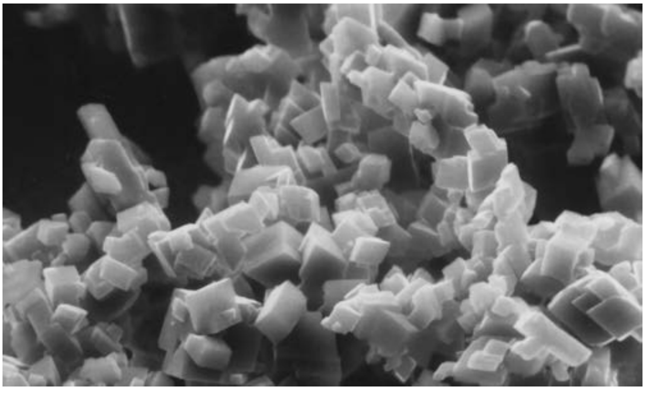


Figure 19.1 Untreated calcium carbonate crystals (2000×).

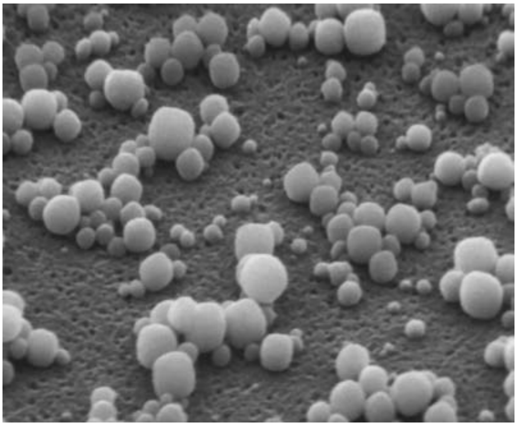


Figure 19.2 Calcium carbonate crystals modified by polyacrylate (2000×).

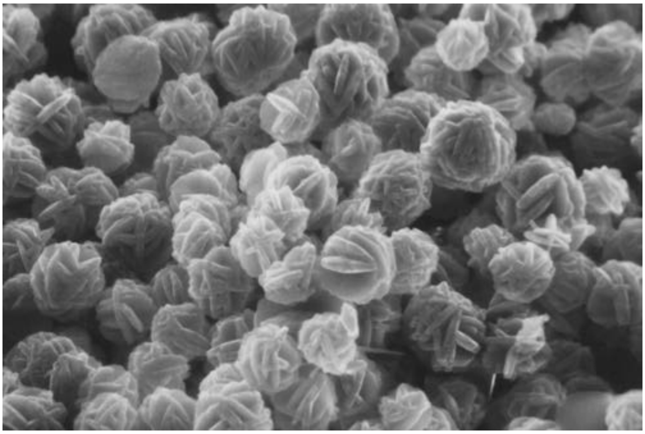


Figure 19.3 Calcium carbonate crystals modified by blend of phosphonate and polyacrylate (2000×).

Other examples include dispersants and scale conditioners. Dispersants can be effective for some forms of scale. If precipitation in bulk solution occurs, particles can be dispersed by polymeric dispersants. Scale conditioners chemically modify the crystal structure of scale, by inclusion of inhibitors into the crystal lattice to form a bulky, loosely adherent, fluid type of deposit, instead of hard scale. Typical conditioning agents are lignins, tannins, and acrylate polymers.

Dispersant Mechanisms

Dispersants are highly charged synthetic polymers that prevent small particles from agglomerating into larger masses, which settle out on surfaces more easily. The mechanism of dispersion is by charge reinforcement or steric stabilization.

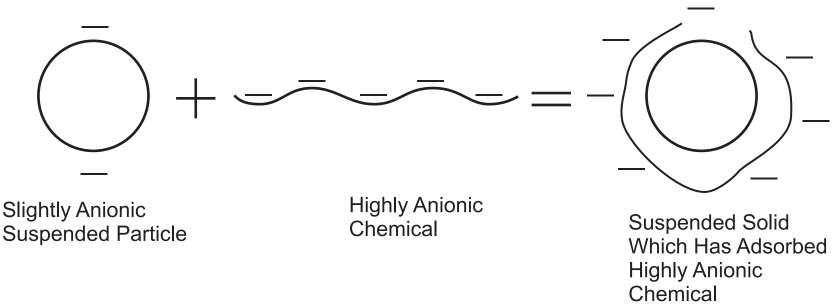


Figure 19.4 Suspended particle adsorbs highly anionic polymer, greatly increasing surface charge.

Dispersion by charge reinforcement increases negative electrical charge that all particles in solution have. Low molecular weight anionic polymers adsorb onto the surface of particles in water increasing the negative charge of the particle. Increased surface charge helps prevent agglomeration and settling of solids (Fig. 19.4).

Adsorbed polymers on the surface of particles also prevent agglomeration by creating a physical barrier to other particles. This barrier acts like an elastic cushion that prevents particles from sticking together. This is called the steric effect and is dependent on the structure and molecular weight of the adsorbed polymer.

Generally, polymers function through both electrostatic repulsion and steric stabilization. When two particles approach each other, steric effects or charge repulsion interfere with agglomeration (Fig. 19.5). Resulting particles remain small enough that a stable suspension is produced. If two particles collide and agglomerate,

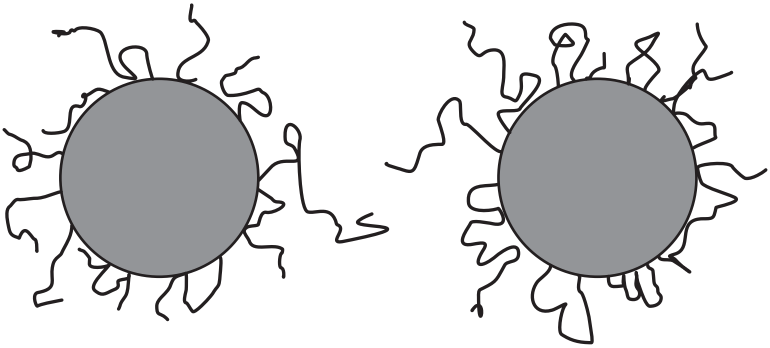


Figure 19.5 As particles coated with polymer approach each other, the polymer can help prevent agglomeration by charge repulsion and steric stabilization.

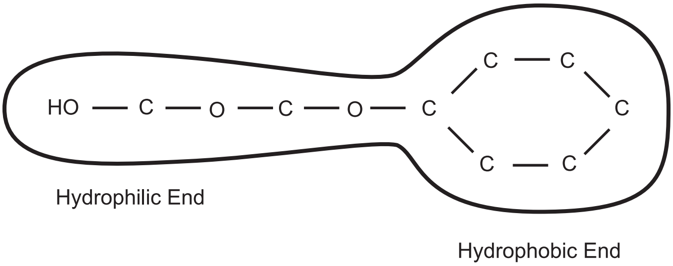


Figure 19.6 Typical surfactant molecule.

particle size increases. As particle size increases, potential for deposition increases.

Surfactant Mechanisms

Surfactant molecules have a hydrophilic end (attracted by water) and a hydrophobic end (repulsed by water) (Fig. 19.6). In cooling water, the hydrophobic end is repulsed by water and forced to concentrate at the water's outer surface. This is how a surfactant reduces surface tension of water. Lower surface tension reduces energy needed to move a particle into the water phase. Particulate matter and organic materials are attracted to the hydrophobic end of the surfactant molecule and carried with recirculating water.

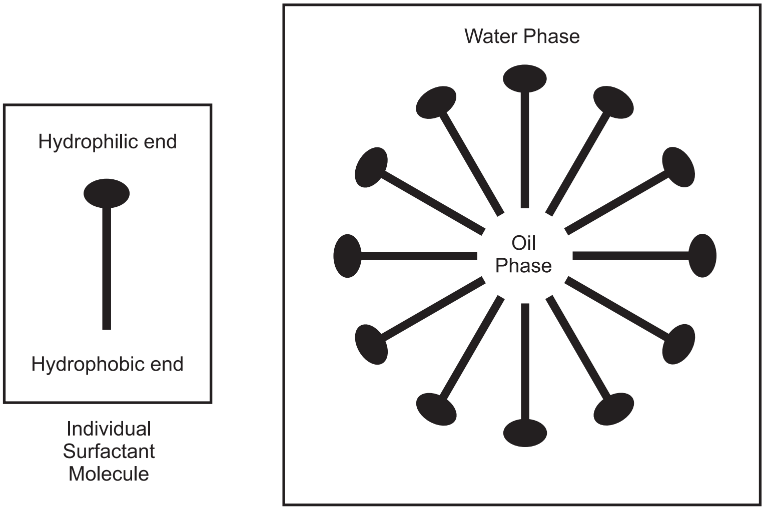
Surfactants form organized clusters, called micelles, around hydrocarbons in water. Micelles occur above a minimum concentration value that is characteristic of each surfactant. When water is the solvent and oil is the material to be emulsified (oil in water), the hydrophobic end is in the oil, and the hydrophilic end is in the water (Fig. 19.7). In a nonaqueous system (water in oil), the reverse is true. This emulsifying mechanism is used to remove process leaks or hydrocarbons that have fouled metal surfaces.

Examples of Deposit Inhibitors

A wide range of chemicals exists that can help to inhibit deposition, either scale or fouling. Many types of phosphate compounds have been used as scale inhibitors for calcium carbonate ($CaCO_3$) and calcium sulfate ($CaSO_4$). Among the most successful have been the phosphonates. Examples of these include amino tris (methylene phosphonic acid) (AMP), 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP), and 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTC).

Polymers

Some polymers are strictly dispersants to prevent deposition of suspended material, and some are both scale inhibitors and dispersants. Polymers used for scale inhibition or dispersant applications are



Individual
Surfactant
Molecule

Surfactant Micelle in Water
Containing Oil Contamination

FIGURE 19.7 Micelles are organized clusters of surfactant molecules in solution. Oil can be emulsified and dispersed by the surfactant micelle.

generally low molecular weight materials (1000–30 000), with a variety of negatively charged functional groups. Polymers can be either homopolymers of one monomer, or copolymers or terpolymers of two or three monomers. Copolymers and terpolymers generally give better performance than homopolymers for the same function, except for calcium carbonate scale control. Copolymers and terpolymers can be optimized for different tasks like calcium phosphate or iron stabilization. Each type of polymer has different properties and performs differently in cooling water systems.

The real benefit of these polymers is the ability to prevent deposition under high stress conditions. Polymers containing sulfonate functionality are generally best at this.

Silica Scale Inhibitors

Application of cost-effective reliable silica inhibitors has long been a goal in the water treatment industry. There are a growing number of applications in the market. Silica control is an active area of investigation and innovation in the water treatment marketplace. Even now, there are inhibitors that prevent silica scale over 200 mg/L levels in the water, and some show effectiveness up to 300 mg/L.

Polymers for Silica Inhibition A variety of polymers are marketed for silica scale control, including a copolymer of acrylic acid and

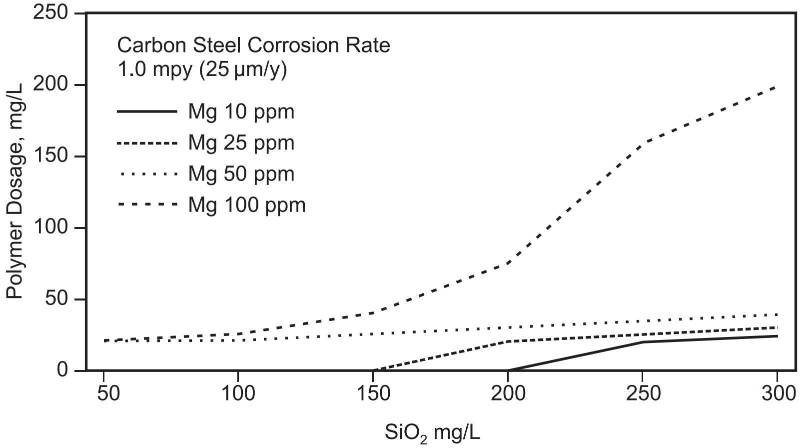


Figure 19.8 Dosage of AA/AMPS/t-BAM polymer needed for various silica and magnesium concentrations.

allyl-hydroxy-propyl sulfonate ether (AA/AHPSE), polyepoxysuccinic acid (PESA), and alkyl epoxy carboxylate (AEC). A promising dispersant is a terpolymer of acrylic acid (AA), 2-acrylamido-2-methylpropylsulfonic acid (AMPS) and t-butylacrylamide (t-BAM). This material is expensive, but it can be effective. An example of the performance of this polymer in preventing silica scale is shown in Fig. 19.8.

Borate Nalco developed the application of borate for maintaining soluble silica in excess of 300 mg/L in cooling water. It is fed at a high level, but is very effective. Dosage depends on silica in makeup water and desired cycles of concentration. Due to environmental discharge limits on boron, application of this technology is limited in some areas.

Surfactants

Surfactants (surface active agents) are organic chemicals with applications in cooling systems that include biodispersants, oil dispersants, and cleaning applications. Surfactants function in the following ways:

- Wetting—reduction of surface tension between two liquids or liquid and solid, so that the two materials make very good contact
- Detergency—breaking adhesion of soils to surfaces and dispersing and suspending particulate soils
- Emulsification—homogenizing grease, oil, or fat into small particles, dispersed evenly into a liquid phase (generally water) by chemical action

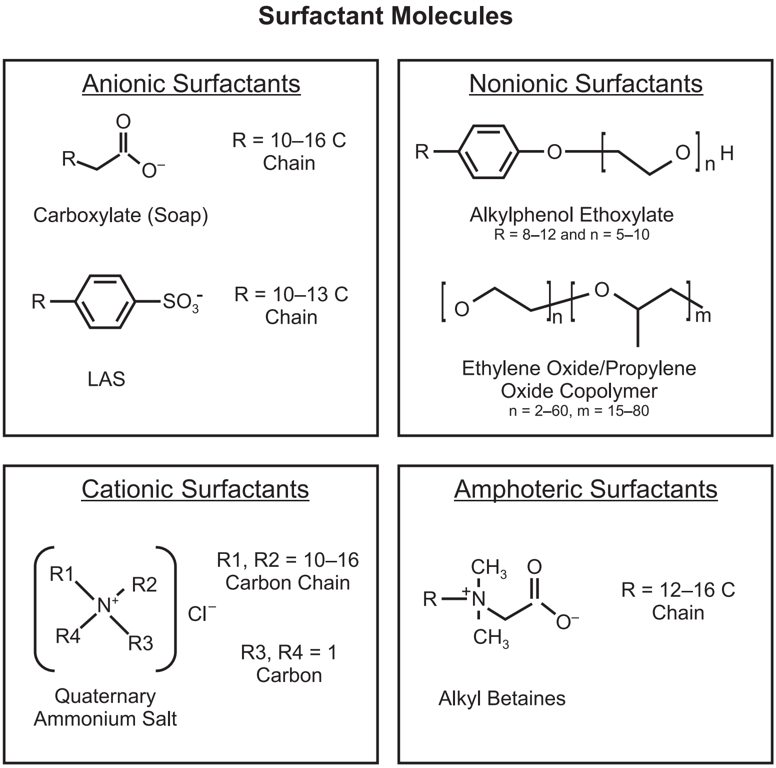


Figure 19.9 Structures of some common surfactants.

There are four basic types of surfactants, examples of which are shown in Fig. 19.9. Anionic surfactants (negative charge) like linear alkyl benzene sulfonate (LAS) are generally the least expensive and oldest known surfactants. However, LAS is not biodegradable, and its use is limited in some areas and countries. Nonionic surfactants (no charge) are used as dispersants and often give better performance with lower foaming than anionic surfactants. Cationic (positive charge) and amphoteric (both negative and positive charge) surfactants are primarily used in fabric softeners, bacteriostats, cosmetics, personal care products, and other specialty applications.

Surfactants can be beneficial in cooling water programs. Materials that reduce interfacial tension between water and bacterial slime layers, can help remove these deposits and make chlorination or bromination more effective. Surfactants can help emulsify oil leaks in refineries and chemical plants, keeping oil dispersed in water. Other types of surfactants can be useful in dispersing soils or suspended solids. Surfactants are not often used on a continuous basis, but may be part of a periodic cleaning program. One caution when using surfactants in cooling towers is the foam that may result. Dosage control is important to minimize foaming, and having antifoam on hand is valuable if undesirable foaming occurs.

Corrosion Control Methods

Corrosion control is a key part of maintaining a cooling water system. The corrosion problem can be the most complex to solve; thus, it is important to know all possible avenues for control. A complete solution involves combination of several possible ways to minimize corrosion. Some common methods include:

- Use of corrosion resistant materials such as stainless steel, copper-nickel alloys, and plastic.
- Applications of coatings or inert barriers such as paint, epoxy coatings, and metal cladding to separate metal from water.
- Cathodic protection, which supplies electrons to metal that would normally corrode. This turns an anodic metal (electron producer) like steel into a cathode (electron supplier), which means the steel does not corrode.
- Sacrificial anodes reduce corrosive attack by electrically coupling a more anodic metal (usually zinc, magnesium, or aluminum) to equipment metal (usually carbon steel).
- Application of chemical corrosion inhibitors as part of a complete cooling water treatment program to reduce corrosion, fouling, and microbial growth.

Knowledge of possible benefits and pitfalls of each solution is important. For example, one might think that using stainless steel in all parts of a system would be the answer to all corrosion problems. However, this would be an expensive solution. Other problems including stress corrosion cracking or pitting of stainless steel may result from high chloride concentration. Either of these could lead to more catastrophic damage than general corrosion on regular carbon steel.

Corrosion Inhibitor Mechanisms

All parts of a corrosion circuit must be completed for corrosion to proceed. This includes anodic and cathodic reactions, conduction of electrons through metal, and flow of ions in solution. Therefore, any chemical applied to water that stops one part of the corrosion reaction reduces corrosion. Chemical inhibitor classification is based on how the inhibitor affects the corrosion cell. Chemical inhibitors, therefore, are put into four general classifications: anodic inhibitors, cathodic inhibitors, combination anodic and cathodic inhibitors (bipolar films), and film-forming inhibitors.

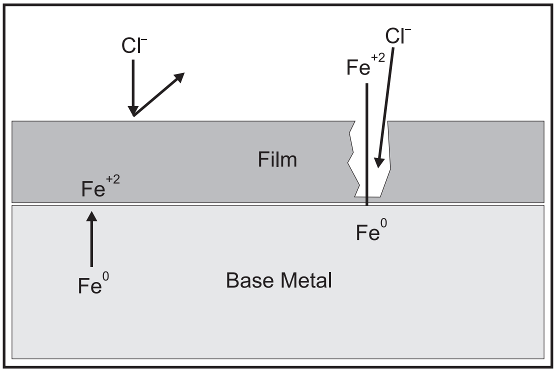


Figure 19.10 An effective anodic film is impermeable to both ferrous ions and aggressive ions in solution like chloride. If there are breaks in the film (right), ferrous ions can be transported into solution, and chloride can penetrate the film, increasing the corrosion rate.

Anodic Corrosion Inhibitors

Anodic corrosion inhibitors function by interfering with the anodic reaction, reducing the rate of dissolution of metal into solution. For example, corroding iron produces ferrous ions and iron oxides. Anodic inhibitors function to either promote formation of protective iron oxide films, or by forming precipitates that improve characteristics of oxide films, in order to reduce both physical and chemical ion permeability. The oxide film must have physical integrity to prevent diffusion of metal ions into solution or prevent ions in solution from penetrating to the metal surface (Fig. 19.10). If the film is permeable or damaged, resulting metal loss is concentrated at the break in the film. This produces high corrosion rates at small anodic sites, and pitting results. Therefore, it is important to maintain sufficient quantities of anodic inhibitor in the system at all times to prevent pitting attack.

Based upon the mechanism of inhibition, anodic inhibitors can be classified into two categories: oxidizing inhibitors or nonoxidizing inhibitors.

Oxidizing Anodic Inhibitors This group (of which nitrite is an example) promotes rapid oxidation of the metal surface to form a thin tightly adherent layer of metal oxides. They do not require oxygen in order to function. On steel, the protective layer is a passive film of gamma iron oxide (FeOOH). Passive films can be very thin and invisible to the unaided eye. These oxidizing anodic inhibitors are called "dangerous" inhibitors when used alone, because pitting problems can occur, if dosage drops below the passivation level.

Nonoxidizing Anodic Inhibitors The second class of anodic inhibitor is not capable of oxidizing ferrous to ferric iron, and requires the presence of oxygen to provide corrosion protection. These inhibitors function by reacting with dissolving metal ions such as ferrous (Fe^{+2}), to form an insoluble salt or complex that precipitates as a film on anodic sites (e.g., iron salts of carbonate, orthophosphate, phosphonate, or molybdate). These materials facilitate formation of an inhibiting film by catalyzing reaction of ferrous iron to ferric oxides, like gamma iron oxide, or these inhibitors chemisorb on the oxide layer, reducing ionic permeability of said layer.

Cathodic Corrosion Inhibitors

Cathodic inhibitors prevent reduction of oxygen or electron transfer at the cathode. Cathodic barrier films need physical and electrical impermeability to prevent oxygen from physically reaching the metal surface, and to prevent electron flow from the metal through the film. Both are needed to prevent oxygen reduction (Fig. 19.11).

Cathodic barrier films are generally catalyzed by hydroxide (OH^-) produced by the cathodic reaction. Localized high pH (measured as high as pH 10–11) at cathodic sites can precipitate various compounds and create an inhibitor film. A zinc-based inhibitor is a good example. When corrosion occurs, the OH^- ions produced decrease solubility of zinc ions in solution, and zinc hydroxide or carbonate precipitates at these high pH sites. As corrosion is reduced, formation of hydroxide decreases, and the growth of inhibiting film is reduced. These inhibitors are generally considered self-limiting film formers.

The challenge of a good cathodic inhibitor program is to allow this pH driven mechanism to occur, while preventing thermally driven precipitation of the inhibitor (Fig. 19.12). Proper polymer selection is essential in designing an inhibitor program for balanced control of pH and thermally driven precipitation. The polymer helps to prevent thermally driven precipitation, while allowing the protective pH driven mechanism to occur.

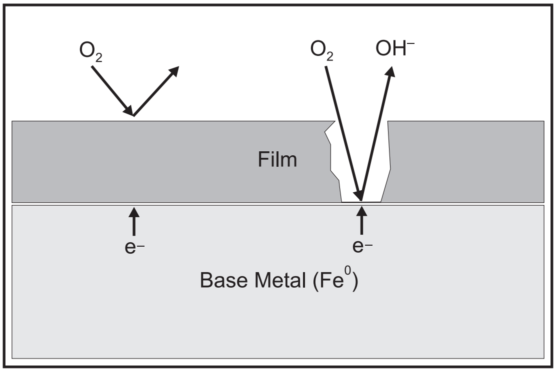


Figure 19.11 An effective cathodic film is impermeable to oxygen and an effective insulator for electron transfer. Breaks in the film allow oxygen penetration and reduction with electrons in the metal, increasing the corrosion rate.

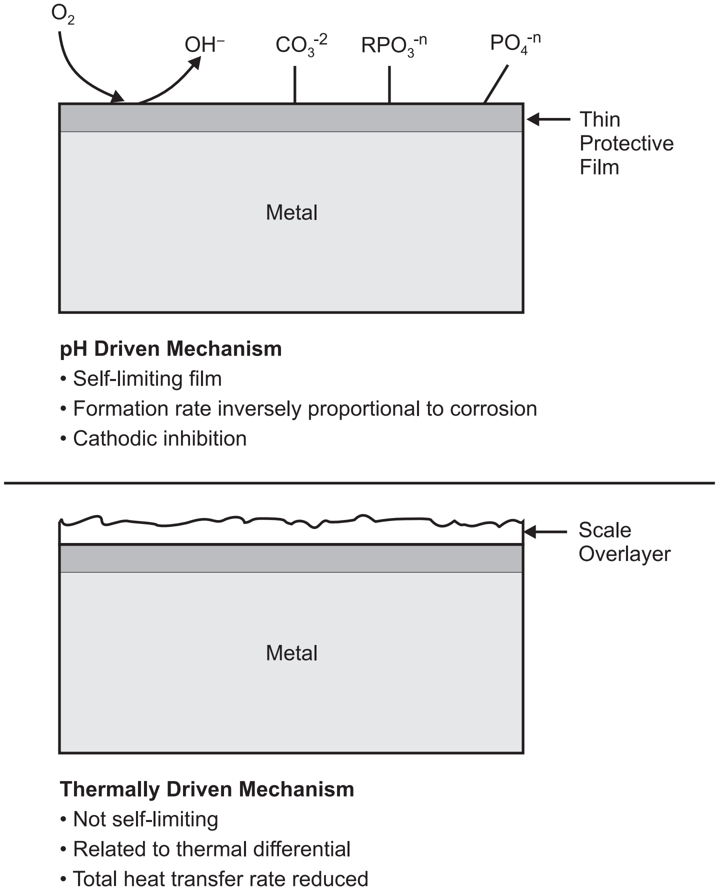


Figure 19.12 Cathodic film formation occurs by a self-limiting pH driven mechanism. Thermally driven precipitation of scale is not self-limiting and is controlled by polymers.

Bipolar Films

Combinations of both anodic and cathodic inhibitors are sometimes called synergistic, since the combination provides lower corrosion rates than either inhibitor alone, even at high levels. Combinations can prevent problems that may occur when using only one type of inhibitor alone, such as pitting that may occur if the concentration of an anodic inhibitor is too low. Inhibitor combinations result in a bipolar film of metal oxides produced by the anodic inhibitor, and a barrier film produced by the cathodic inhibitor, simply represented by two layers on a metal surface (Fig. 19.13). The oxide layer prevents dissolution of base metal, and the barrier film prevents transfer of electrons and reduction of oxygen.

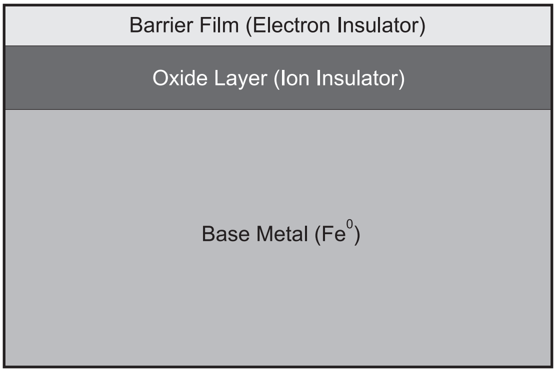


Figure 19.13 The strongest corrosion inhibiting films combine properties of anodic oxide layers with cathodic barrier films.

Film-Forming Inhibitors

While all inhibitors form a layer of some kind, some inhibitors produce an inhibitor film on the metal surface mostly by adsorption, which limits corrosion. This category includes organic materials that maintain a barrier between the water and metal surface to prevent corrosion. An inherent danger in the film-forming approach is that a small break in the continuous film could allow the corrosive agent to attack the unprotected area, resulting in rapid metal penetration. Therefore, filming inhibitors must be continuously fed to cooling systems to maintain the protective film. Azoles fall into this category.

Examples of Corrosion Inhibitors

An effective corrosion control program usually depends on specific inhibitors for reducing the anodic reaction, the cathodic reaction, or both. Common inhibitors used for corrosion protection in cooling water systems are shown in Table 19.1. Most inhibitors may exhibit both anodic and cathodic characteristics, but the principal mode is primarily anodic or cathodic.

Principally Anodic	Principally Cathodic	Both Anodic and Cathodic
Nitrite	Carbonate	Azoles
Orthophosphate	Polyphosphate	Phosphonates
Bicarbonate	Zinc	Organic filming amines
Silicate		
Molybdate		

Table 19.1 Typical Corrosion Inhibitor Classification

A variety of anodic inhibitors exists, most of which are nonoxidizing. Their properties vary based on chemistry of their interaction with iron.

Zinc and polyphosphate are cathodic corrosion inhibitors commonly used in cooling water systems. Since they are cathodic inhibitors, they can be effective on more metals than just iron or steel. This is because interaction with the cathodic reaction (hydroxide production) is the same for all metals.

Zinc Zinc-based programs have been used for many years. A typical alkaline zinc program combines cathodic protection of zinc with anodic inhibition of orthophosphate, to operate at low zinc levels (0.5–2.5 mg/L) and pH ranging from 7 to 9. These programs use specialized polymers for stabilization of zinc in solution. Zinc is a cost-effective corrosion inhibitor and is used in many different types of applications. Corrosion inhibition is provided by positively charged soluble zinc ions (Zn^{+2}), which are attracted to the negative ionic environment at cathodic surface sites, and form a film that prevents oxygen reduction. Environmental restrictions may limit use of zinc in some applications and some regions of the world.

Polyphosphates Polyphosphates, described earlier in this chapter as stabilizers of calcium carbonate, are also corrosion inhibitors. Polyphosphates require the presence of a divalent ion such as calcium to function as a corrosion inhibitor. Calcium polyphosphate can precipitate at the cathode, due to limited solubility at the localized high pH. To effectively form calcium polyphosphate film, calcium must be present at sufficient concentration. Depending upon the polyphosphate used, the minimum concentration of calcium is typically 50 to 100 mg/L as $CaCO_3$.

Combined Anodic and Cathodic Inhibitors

Depending on water chemistry, some phosphonate (organic phosphate) scale inhibitors can function as both anodic or cathodic inhibitors. Phosphonates as corrosion inhibitors are common in all-organic treatment programs operating at highly alkaline conditions. In the anodic reaction, phosphonates catalyze oxidation of ferrous hydroxide to gamma iron oxide (FeOOH). As with orthophosphate, the presence of oxygen is required. As cathodic inhibitors, calcium phosphonates can precipitate to form a barrier film on the metal surface. The film can be a coprecipitate with calcium carbonate, depending on pH and water chemistry. The first phosphonates commonly used in these applications were AMP, HEDP, and PBTC (described earlier in this chapter for their ability to control calcium-based scale). Some phosphonates that are more effective on corrosion include PCA (phosphino-carboxylic acid) and HPA (hydroxyphosphono-acetic acid), and PSO (phosphino succinic oligomer).

Inhibitor	Corrosion Rate at 15 mg/L Active	Corrosion Rate at 30 mg/L Active
No inhibitor (Blank)	44 mpy (1118 μm/y)	44 mpy (1118 μm/y)
PSO	2.5 mpy (64 μm/y)	1.0 mpy (25 μm/y)
HEDP	13 mpy (330 μm/y)	8.1 mpy (206 μm/y)
AMP	9.3 mpy (236 μm/y)	16 mpy (406 μm/y)
PBTC	6.2 mpy (157 μm/y)	10 mpy (254 μm/y)

Test Conditions: 360 mg/L $CaCl_2$ (as $CaCO_3$), 200 mg/L $MgSO_4$ (as $CaCO_3$), 100 mg/L $NaHCO_3$, pH 8.4, 120°F (49°C), 160 rpm, 16-hour immersion.

Table 19.2 Corrosion Inhibition Screening Tests of Phosphonates

PCA has a C—P—C bond instead of the C—P—O bond of more common phosphonates. Depending on structure, these can be optimized as dispersants or as corrosion inhibitors. HPA is a specific PCA that is a very effective corrosion inhibitor and has been used in all-organic programs. It is expensive and very sensitive to chlorine. It is not widely used in large cooling tower systems.

PSO was originally developed as a scale inhibitor but has excellent corrosion inhibiting properties as well. It is stable to halogens even at high dosage (up to 5 mg/L halogen). The mechanism of action is primarily cathodic, but it has anodic inhibition characteristics as dosage increases. As a cathodic inhibitor, PSO functions by precipitating a calcium-PSO or iron-PSO film, similar to pyrophosphate, at cathodic areas. Anodic function is similar to other phosphonates that work with oxygen to form gamma iron oxide. PSO yields much lower corrosion rates than other phosphonates as shown in Table 19.2.

Film-Forming Inhibitors

Typical film-forming inhibitors include azoles and thiazoles applied to reduce copper and copper alloy corrosion. These organic compounds are chemisorbed onto the metal surface and form thin protective films. In addition to corrosion protection, they form complexes with soluble copper in solution and prevent redeposition of copper metal onto other surfaces. Azoles are incorporated into a wide range of programs for both closed and open systems.

The most common azoles are benzotriazole (BZT) and tolyltriazole (TT or TTA). BZT and TT are both relatively stable under conditions of typical cooling water conditions. Alkyl benzotriazoles have been proposed to form more stable, longer lasting films. Two examples are butyl benzotriazole (BBT) and pentoxy benzotriazole (POBT).

Chloro-tolyltriazole has been used as a halogen resistant azole (HRA). This material was introduced to minimize problems with TT

Figure 19.14 Structure of chloro-tolyltriazole.

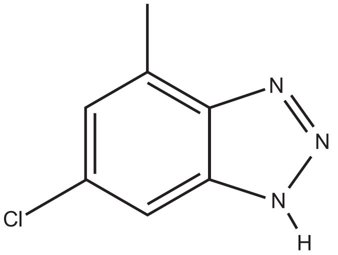
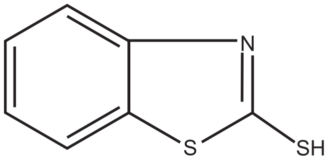


Figure 19.15 Structure of mercaptobenzothiazole.



application in heavily chlorinated systems. Chlorination of the benzene ring (Fig. 19.14) in HRA minimizes reaction of chlorine with nitrogen atoms in the azole ring.

One of the earliest azoles used was mercaptobenzothiazole (MBT), but it is not used widely today. MBT (Fig. 19.15) provides excellent copper corrosion inhibition. The molecule reacts with copper surfaces via the –SH group to form a barrier film. This copper corrosion inhibitor is the fastest film former of the azoles. It is useful well above the boiling point of water. Microorganisms degrade the molecule rapidly, while halogens and oxygen oxidize the –SH group rapidly. MBT finds widespread use primarily in closed and once through cooling water systems, where these degradation pathways are less problematic.

Biological Control Methods

Control of biological growth in cooling systems requires a management approach that considers the mechanical aspects, chemical characteristics, and operation of the system. Many of these factors were described in Chap. 17. This section covers chemical control of microorganisms in cooling systems. Because of biocide toxicity to other organisms in the environment, any control method that minimizes the amount of biocide used is valuable. In the future, less toxic methods of control will be more desirable.

Control of microbiological contamination is not simply choosing the right biocide, rather it is a program to control biofouling. This program requires in-depth understanding of the cooling system, and includes taking measures to exclude harmful microorganisms and environmental and process contaminants. The program also uses biocides, and dispersants, as well as filtration to remove suspended solids, and must include a firm plan, to monitor effectiveness and reduce biological diversity.

Oxidizing Biocides

Oxidizing biocides include chlorine, bromine, chlorine dioxide, ozone, chlorine or bromine slow-release compounds, stabilized halogens, peroxide and peroxyacetic acid. Although there are differences among these materials, their primary mode of action is to oxidize compounds in microorganisms. Chlorination is an oxidizing reaction; however, we need to note that oxidation is not always chlorination. This insight will be useful later in this section. No organism has ever been shown to develop resistance to an oxidizing biocide. Oxidizers are effective against all types of microorganisms in cooling systems, including bacteria, fungi, algae, and yeast.

Chlorine and Hypochlorite

Generally, chlorine is supplied as chlorine gas (Cl_2), dissolved in sodium hydroxide as sodium hypochlorite (NaOCl), or as a solid like calcium hypochlorite [$Ca(OCl)_2$]. When chlorine gas is dissolved in water, it produces hypochlorous acid (HOCl) and hydrochloric acid (HCl) as in Eq. (19.1). Hypochlorous acid dissociates in water to produce hypochlorite ion (OCl^-) and hydrogen ion (H^+) as shown in Eq. (19.2). Sodium hypochlorite or calcium hypochlorite produce HOCl when diluted in cooling water [the reverse reaction in Eq. (19.2)]. Hypochlorous acid is the active biocide when either chlorine gas or hypochlorite is introduced into water. Hypochlorite ion is a less effective biocide than HOCL.

$$Cl_2 + H_2O \rightarrow HCl + HOCl \tag{19.1}$$

$$HOCl \rightleftharpoons H^+ + OCl^- \tag{19.2}$$

System pH affects the amount of HOCl present and thus biocidal effectiveness of chlorine in a cooling water system. As pH increases, percent of hypochlorous acid decreases as shown in Fig. 19.16. As the curves indicate, the percent of hypochlorous acid is limited above pH 8. As temperature increases, the amount of HOCl at a given pH decreases. Therefore, chlorine is most effective in systems that operate near neutral or slightly alkaline pH.

Hypochlorous acid can also be produced electrochemically from a sodium chloride solution. This process is sometimes more expensive than purchasing sodium hypochlorite since equipment, maintenance, and power costs may be significant. This method is often used in situations where seawater is available, or sodium hypochlorite is difficult to obtain, or environmental concerns regarding storage of chemicals is paramount.

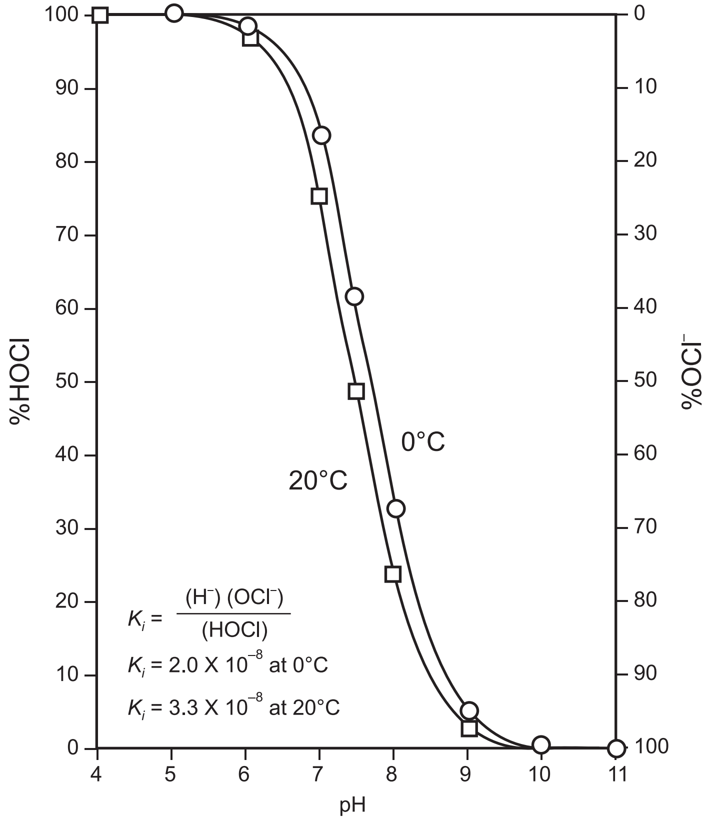


FIGURE 19.16 Dissociation of hypochlorous acid versus pH.

Chlorine-Release Compounds and Stabilized Halogens

A variety of organic compounds releases hypochlorous acid when dissolved in water. These chemicals are easier or safer to feed than gaseous or liquid chlorine compounds. Organic compounds that are available, vary in stability, product form, cost, and chlorine-release mechanism. One chlorine-release compound that has relatively good stability and safety characteristics is sodium dichloroisocyanurate dihydrate. Figure 19.17 shows the reactions that release hypochlorous acid when added to water. Another stabilized chlorine compound is produced when sodium sulfamate is added to a bleach solution. The chlorosulfamate formed in this process serves to release HOCl in water [Eq. (19.3)].

$$\mathrm{ClHNSO_3Na + H_2O \rightarrow HOCl + H_2NSO_3Na} \tag{19.3}$$

Bromine

Bromine undergoes the same reactions as chlorine. Bromine dissolves in water to form hypobromous acid (HOBr), which dissociates to

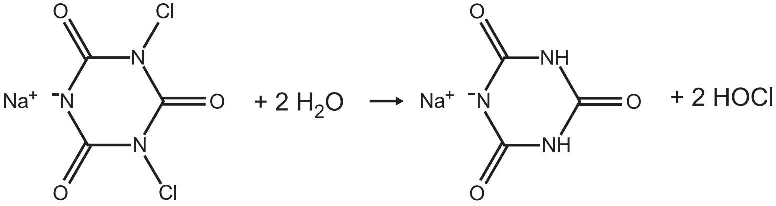


Figure 19.17 Chlorine-release mechanism of sodium dichloroisocyanurate dihydrate.

give an equilibrium mixture of hypobromous acid and hypobromite ion (OBr^-). HOBr is similar in biocidal activity to HOCl. The major advantage of bromine over chlorine is that more HOBr is available at higher pH and temperature (Fig. 19.18). Therefore, in systems that operate at pH above 7.5, bromine is a more effective biocide than chlorine.

Bromine is a liquid at normal ambient pressure and temperature and not a gas like chlorine. Handling and feeding liquid bromine to cooling systems creates safety concerns. In addition, concentrated sodium hypobromite (NaOBr) solutions are not stable because NaOBr decomposes rather quickly. Three safe ways to use bromine biocides are:

1. On-site HOBr generation can be cost-effectively done by mixing a solution of sodium bromide and a chlorine source such as sodium hypochlorite. The reaction to produce HOBr is very fast, and varying ratios of chlorine to bromine actives can be produced.

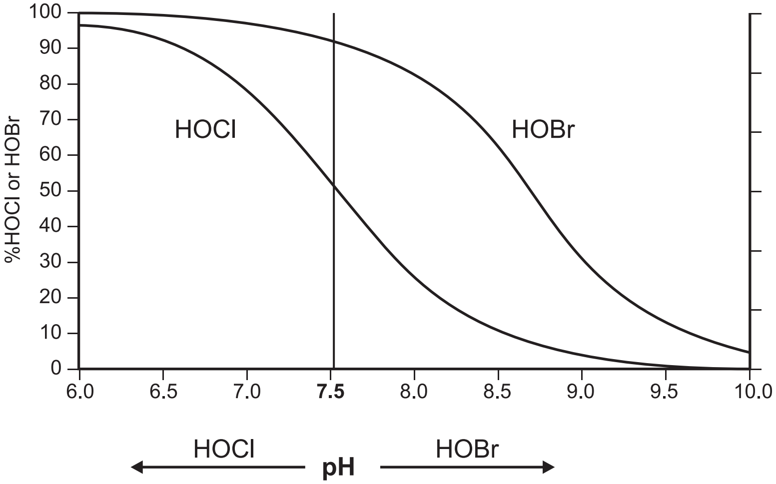


Figure 19.18 More active HOBr is available at any given cooling water pH compared to active HOCl.

2. Bromine-release compounds like bromo chloro dimethyl hydantoin (BCDMH), which generates both HOBr and HOCl in water, can be used. Solid BCDMH requires a dry feed system, using makeup water to dissolve the product.
3. Stabilized bromine products involve a combination of NaOBr and a stabilizer. The result is a stable liquid product that is relatively safe and easy to feed to cooling systems. In cooling water, the stabilizer releases bromine as HOBr is consumed.

Non-Biological Halogen Consumption Chlorine and bromine can be consumed by other materials in cooling water that reduce availability for biological control. Ammonia, organics, and even some treatment components react with chlorine and bromine.

Reaction of chlorine with ammonia in cooling water, or in onsite generators, to form chloramines (combined chlorine) is one of the most common reactions. Depending on the amount of chlorination and ammonia concentration, monochloramine [Eq. (19.4)], dichloramine [Eq. (19.5)], or trichloramine [Eq. (19.6)] may be formed. Chloramines are less effective biocides and do not kill as quickly as HOCl.

$$\mathrm{HOCl} + \mathrm{NH_3} \rightleftharpoons \mathrm{H_2NCl} + \mathrm{H_2O} \tag{19.4}$$

$$\mathrm{HOCl} + \mathrm{H_2NCl} \rightleftharpoons \mathrm{HNCl_2} + \mathrm{H_2O} \tag{19.5}$$

$$\mathrm{HOCl} + \mathrm{HNCl_2} \rightleftharpoons \mathrm{NCl_3} + \mathrm{H_2O} \tag{19.6}$$

Cooling water treatment components can also react with chlorine. Phosphonates used as corrosion and scale inhibitors along with some azoles used for copper alloy corrosion protection can react with halogens. Some chlorinated azole compounds are volatile and can be stripped from water passing over the cooling tower. Reaction of chlorine with organic contaminants produces nonvolatile chlorinated organics, commonly called adsorbable organic halides (AOX), (adsorbable onto activated carbon). AOX is environmentally undesirable, since a number of halogenated hydrocarbons are toxic.

Chlorine Dioxide

Chlorine dioxide (ClO_2) provides excellent microbial control. Advantages and disadvantages are shown in Table 19.3. ClO_2 must be generated on-site by chemical or electrochemical methods, although systems with relatively low demand can be treated with available low concentration liquid products. The most common production methods of on-site generation are reaction of sodium chlorite ($NaClO_2$) with one of several acids [Eq. (19.7)], reaction of sodium chlorate with acid

Advantages of Chlorine Dioxide	Disadvantages of Chlorine Dioxide
Effective biocide	Generally generated on-site, except for limited volumes
Activity does not decrease at high pH	Training and monitoring costs are significant
Does not react with ammonia or amines	Cost of production ranges from moderate to high
Works well in high chlorine demand systems	Volatile and easily stripped from open systems
Does not react significantly with organics to produce AOX	Handling reactants is a safety concern

Table 19.3 Chlorine Dioxide Considerations for Cooling Systems

(in the presence of a reducing agent), or the reaction of sodium chlorite with chlorine or bleach [Eq. (19.8)].

$$5NaClO_2 + 4HCl \rightarrow 4ClO_2 + 5NaCl + 2H_2O \tag{19.7}$$

$$2NaClO_2 + Cl_2 \rightarrow 2ClO_2 + 2NaCl \tag{19.8}$$

Sodium chlorite can also be converted electrochemically to ClO_2 in a continuous process. However, compared to chemical methods, equipment and maintenance costs can be high.

Peroxides

Hydrogen peroxide (H_2O_2) and peracetic acid (CH_3CO_3H) are sometimes used as biocides. Hydrogen peroxide is a very strong oxidant with well-known antimicrobial properties, but it can be consumed in many ways in cooling water (meaning it reacts with almost anything capable of being oxidized, thus high doses may be required). It is not persistent, and often requires multiple feed points to achieve results. Therefore, it has often shown poor performance in preventing microbial fouling. H_2O_2 has several environmental advantages, including no AOX formation, no reaction with amines, and end products are water (H_2O) and oxygen (O_2).

Peracetic acid (PAA) dissociates in water to produce hydrogen peroxide and acetic acid (CH_3CO_2H) [Eq.(19.9)]. PAA has potential as a cooling water biocide since it is a powerful oxidant (second only to ozone), and H_2O_2 contributes some capability. It is effective as high as pH 9.5, but optimum activity is achieved below pH 8.6. PAA has similar advantages to H_2O_2; main disadvantages are high cost and safety concerns of the concentrated product.

$$CH_3CO_3H + H_2O \rightleftharpoons H_2O_2 + CH_3CO_2H \tag{19.9}$$

Ozone

Ozone (O_3) is produced by passing oxygen or air through a corona discharge electric field. It readily dissolves in water and is a strong oxidant with several potential benefits. Ozone is one of the strongest oxidizers known, meaning it reacts with almost anything that can be oxidized, therefore resulting in high feedrate. Ozone can be an effective biocide and offers potential for being convenient, safe, and environmentally friendly. It is generated on-site, and there is no inventory of hazardous biocides. If applied properly, ozone is totally consumed in the cooling system, and ozone does not produce halogenated organics (AOX). Therefore, little or no discharge of any toxic chemicals occurs.

Ozone has important disadvantages, which have limited its application as a cooling water biocide. The half-life of ozone in cooling water is very short, and it is difficult to ensure that ozone reaches all areas of the system. As with peroxide, multiple feed points are often required. Ozone generators are expensive, and maintenance costs are high. Cost can be several times the annual water treatment chemical cost for a given system. Ozone reacts with many organics, and it can degrade components of the cooling system. Finally, ozone can increase metal corrosion rates and remove zinc from alloys.

Use of ozone has been proposed periodically as a total treatment option for cooling towers. Ozone is claimed to provide control of deposition, corrosion, and microbial fouling, sometimes while operating with zero intentional blowdown. The foundation of the claim is that if surfaces are kept clean and free of biofouling, prevention of scale, corrosion, and fouling is easier. However, if low corrosion occurs in ozone treated systems, it is most probably due to high alkalinity and pH that results when water is concentrated. Research has shown that ozone has no effect on precipitation of mineral scale and does not affect crystal morphology. Any minimization of scale on heat exchangers in ozone treated systems is again due to operating conditions and not ozone. After long use, scale may build up in the tower fill (low-flow area) rather than on heat exchangers (high-flow areas). Thus, observation that ozone is preventing scale and corrosion is more perception than reality.

Nonoxidizing Biocides

This is a large class of organic compounds that interfere with metabolism of microorganisms, inactivate cellular enzymes, bind cellular proteins, or disrupt cell walls. Biocides for cooling water are typically organic sulfur, nitrogen, chlorine, or bromine compounds. Unlike oxidizing biocides, nonoxidizers are most effective when applied in slug dosages. Many nonoxidizing biocides exhibit activity only toward bacteria, fungi, or algae and not all three. The pH of water has a dramatic influence on specificity and activity of each biocide. There is a wide range of compounds available, a few of which are described in Table 19.4.

Biocide	Mechanism	Advantages	Disadvantages
Isothiazoline	Penetrates cell membrane to deactivate enzymes needed for cell to survive	Effective on both bacteria and fungi, persistent in system, synergism with oxidizers, activity over wide pH range	Inactivated by sulfide contamination, concentrated isothiazoline is a skin sensitizer
Glutaraldehyde	Crosslinking of two adjacent amino groups in cell wall proteins impairs cell function	Very effective in normal pH range of cooling water systems	Reacts with halogens, ammonia, and organic amines (but not quaternary amines), should not be applied in systems with these contaminants or with oxidizing biocides
2,2-dibromo-3-nitrilo propionamide (DBNPA)	Reacts with cellular membranes and enzymes, causing disruption of cell metabolism	Fast acting against bacteria	Lack of persistence, rapid hydrolysis at high pH (Fig. 19.19), high cost relative to other biocides, less effective for algae and fungi
Quaternary ammonium compounds (Quats)	Binds anionic components of cells and cell walls	Generally effective against bacteria, fungi, and algae, have surface-active dispersing properties	Can cause foaming and can inactivate anionic polymer dispersants

Table 19.4 Examples of Some Nonoxidizing Biocides

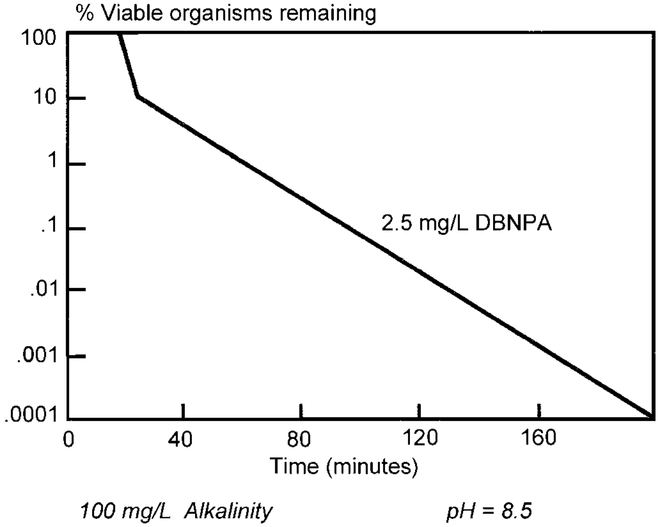


Figure 19.19 Efficacy of DBNPA at pH 8.5.

Algaecides

Algae are metabolically and structurally different from bacteria and often are more difficult to control with common biocides. Terbuthylazine is used specifically as an algaecide. This material interferes with photosynthesis and is very effective at low dosages against algae. However, it has no effect on non-photosynthetic microorganisms (bacteria or fungi). Up to two weeks is needed for control of algae. Terbuthylazine is much more effective when used for prevention rather than controlling existing algae problems.

Copper sulfate has long been used in water to kill or prevent algae growth. The apparent action of copper (as Cu^{+2}) on algae, is blocking transport of oxygen through cell membranes, leading to death. Inner cell protoplasm is released, giving off a characteristic odor. When copper sulfate is added to algae-laden water, algae are killed almost instantly, but considerable time may be required for disappearance of dead plants and associated foul odors. At normal dosages, copper sulfate is also effective against bacteria such as *Gallionella*, which causes iron deposits and "red water." This product is useful for algae control in ponds but must not be used for cooling water systems because of galvanic corrosion that copper ions can cause on mild steel.

Biodispersants and Biodetergents

Biodispersants and biodetergents can improve cooling system microbial control and are an important aspect of complete biocontrol programs. These products do not kill microorganisms but help break up biofilms and suspend bacteria in water, so that they are more readily killed by biocides. Dispersants may prevent or delay attachment of microorganisms to heat transfer surfaces. The primary characteristic of biodispersants is their ability in maintaining clean system surfaces.

Biodispersants and biodetergents are typically nonionic surfactants, though some anionic surfactants are used. They are usually used in conjunction with oxidizing and nonoxidizing biocides to enhance effectiveness. They can be used with all open recirculating and once through system treatments including corrosion inhibitors, scale inhibitors, biocides, and dispersants. They are effective over a wide pH range and are thermally stable at typical cooling water temperatures. As with any surfactant, overfeed of biodispersants can result in foaming and require application of a defoamer. However, use of antifoam can reduce effectiveness of the biodispersant.

Macrofouling Control

Macrofouling attachment of mollusks to piping and other surfaces of a cooling system was described in Chap. 5. The many physical and chemical approaches to mollusk control can generally be divided into methods that prevent infestation of mollusks, or eradicate mollusks once they have grown in a system (Table 19.5). Prevention methods must be applied during the time when mollusks spawn, producing free-floating veligers that can be killed more easily than adult mollusks. Eradication involves killing and removing adult mollusks from a system.

Eradication can involve killing mollusks with biocides, but shells that plug the system must be removed by physical methods. Thermal shock can achieve 100% mortality of most mussels when water

Method	Advantages	Disadvantages
Eradication	Treatment needed only 1–3 times per year Potentially lower chemical cost	Under-deposit corrosion can occur where mollusks attach to system Potentially higher maintenance cost to remove mollusk shells Mollusk shells cause flow restriction
Prevention	No mollusk shells to remove Lower under-deposit corrosion potential (fewer mollusks in system) Generally helps to provide better overall biocontrol in system	Potentially higher chemical cost Must treat more often, generally throughout warm weather months Potentially higher capital cost for feed and detoxification equipment

Table 19.5 Comparison of Macrofouling Control Methods

temperature of 104°F (40°C) is held for 30 minutes. Unfortunately, most facilities are not configured to apply thermal treatment, with the exception of some electric power generating plants.

Both oxidizing and nonoxidizing biocides are used for either prevention or eradication of macrofouling. Chlorine, bromine, chlorine dioxide, and ozone have all been used, with chlorine being most common. Disadvantages of chlorine are mainly environmental concerns and its corrosive nature. Dehalogenation may be required before discharge. The most cost-effective nonoxidizing biocides are quaternary ammonium compounds (quats). These compounds are toxic to many aquatic organisms (like fish), and removal from discharge water by adsorption on clay may be needed.

Amine salts of carboxylic acids have been used with success. One amine/acid combination uses *N,N*-dimethylalkyl amine and endothall (a dicarboxylic acid). The amine is not a quaternary ammonium compound, and it does not have a permanent positively charged nitrogen. Because of this, *N,N*-dimethylalkyl amine has lower water solubility than quaternary ammonium compounds. This limited solubility makes this type of amine a "film former" that coats surfaces in a system. The advantage this offers is that detoxification of the discharge water with clay is not necessary, since the active compound is depleted from water quickly.

Cooling Water Treatment Programs

Most cooling water treatment products contain combinations of cathodic and anodic inhibitors along with scale inhibitors and dispersants. These products, used in combination with biocontrol chemistry, comprise a complete approach to system treatment. Tolerance to fluctuations of system control parameters, such as pH or conductivity, can be very valuable in a treatment program. In the event of severe upsets, the ability of a treatment program to recover quickly when conditions return to normal, is essential. While every program offers different performance in this regard, combinations of anodic and cathodic inhibitors generally provide better performance.

An optimum treatment program generally can be selected for a given system, based on system parameters and water chemistry. Once the program is applied, proper monitoring and control are required for success.

Stabilized Phosphate Programs

These programs are a blend of orthophosphate, polyphosphate, and phosphonates that provide corrosion inhibition for mild steel. Stabilized phosphate programs rely on orthophosphate for anodic inhibition and polyphosphate for cathodic inhibition. Phosphonates prevent calcium carbonate scale, and one of the triazoles is generally included for copper corrosion protection. The key to success depends on special polymers that can stabilize calcium phosphate in cooling water systems.

Stabilized phosphate programs typically operate at 6 to 15 mg/L orthophosphate (PO_4) and up to 20 mg/L total phosphate concentration. Use of softened water and/or low alkalinity can require even higher phosphate residuals. Close control of system pH is required in the range of 6.8 to 8.5 for optimum corrosion and scale control. Therefore, acid is often fed for pH control. Often, simply lowering pH with acid can provide for calcium carbonate scale control, allowing higher cycles to be run, even with a phosphate program. However, even at this moderate pH, calcium phosphate is insoluble, and a calcium phosphate stabilizing polymer must be included.

This program requires calcium for corrosion inhibition and is subject to pitting problems in soft water. Stabilized phosphate programs require good control of pH, calcium concentration, phosphate dosage, and the ratio of orthophosphate to polyphosphate in the cooling system. Stabilized phosphate programs are not suitable for use when high soluble iron is found in makeup water or in systems with a long holding time index. Some regions or countries have strict phosphate discharge limitations that prevent use of traditional stabilized phosphate programs.

All-Organic Programs

These products are designed to provide corrosion inhibition, scale control, and dispersancy without any inorganic corrosion inhibitors like zinc or phosphate. Typical all-organic products are a combination of phosphonates, triazole, and stabilizing polymer. Anodic and cathodic inhibition is provided by the phosphonates, assisted by alkalinity from operating at high pH (> 8.5). Phosphonates provide calcium carbonate scale prevention, and the polymer prevents excessive precipitation of calcium phosphate. Both calcium and alkalinity are required for optimum performance.

An advantage of all-organic programs is that acid for pH control is not typically used. Control of chlorination is equally important to the success of all-organic programs. High free chlorine residuals (> 0.5 mg/L) degrade some phosphonates to orthophosphate, increasing potential for calcium phosphate deposition. As a result, control of product dosage, alkalinity, concentration ratio, and chlorine residuals are very important to the success of this program.

Alkaline Zinc Programs

Zinc can be combined with orthophosphate, phosphonates, or polyphosphate (or mixtures of these) for corrosion protection. The same polymers that are often used for stabilized phosphate or all-organic programs, are used to stabilize zinc in cooling water. These programs can operate at alkaline conditions up to pH 9, because polymers provide zinc and phosphate stabilization. Phosphonates function as scale inhibitors as well as help with corrosion inhibition. Most programs include one of the triazoles for copper corrosion inhibition.

One of the best combinations is zinc, orthophosphate, and triazole, which is generally applied at alkaline conditions. This combination provides cathodic protection from zinc and primarily anodic protection from orthophosphate. Strong cathodic inhibition provided by zinc allows this program to work in very soft water, where stabilized phosphate does not perform as well.

Alkaline Phosphate Programs

In some areas, environmental restrictions allow phosphate for corrosion control, but not the high levels of a traditional stabilized phosphate program. Some facilities do not allow acid for pH control or zinc for corrosion control. In these cases, an alkaline phosphate program may be applicable, because of operation at lower phosphate levels and higher pH and alkalinity. Original programs were a combination of phosphonate, orthophosphate or polyphosphate, triazole, and phosphate stabilizing polymer. Other programs may use phosphonates (organic phosphates), giving the advantage of lower phosphate levels. Organic phosphates like PSO can provide corrosion and scale inhibition. Alkalinity in cooling water provides some buffer capacity in the event of pH swings. The PSO/orthophosphate combination can operate over a wide pH window.

Molybdate Programs

Molybdate is used mainly as a very effective corrosion inhibitor in closed loops, at high residual levels. However, it had been also used in open recirculating tower systems sparingly due to high costs. It has been used most often in combination with other corrosion inhibitors or used at high levels. Molybdate has shown beneficial properties for reducing localized or pitting corrosion. Most molybdate programs use dosages of 5 to 20 mg/L of molybdate in cooling tower systems. This may be combined with orthophosphate or zinc at up to 5 mg/L applied dosage. Phosphonates are used for scale inhibition, and polymers are included to prevent precipitation of phosphate and zinc. Combinations with zinc or phosphate can function at lower pH, calcium, and alkalinity like an alkaline zinc program. Other combinations such as molybdate and phosphonate can be used under more alkaline conditions, similar to an all-organic program.

Non-Phosphorous Programs

Some countries have effluent restrictions that strictly limit phosphate discharge or even tax a company based on its phosphate discharge. For this reason, non-phosphorous (non-P) programs are needed;

however, they are not yet widely used. Non-P programs are typically based on polymers for scale and deposit control with zinc or molybdate for corrosion control. Polymers can include simple polyacrylates, which provide $CaCO_3$ scale inhibition, and copolymers or terpolymers for zinc stabilization. Water chemistry and system operating conditions depend on the combination of inhibitors in the programs. In general, $CaCO_3$ scaling stress (pH, temperature, calcium, and alkalinity) must be lower than when using conventional phosphonate programs. Corrosion capabilities depend on levels of zinc or molybdate (or both) that are fed to the system. In general, corrosivity of system water must be lower than with an alkaline zinc program.

Nonchemical Devices

No discussion of cooling system treatment would be complete without inclusion of nonchemical devices. These include magnetic devices, electrostatic devices, frequency generators, and a host of other nonchemical treatment methods. The lure of these devices is obvious; install a simple mechanical device and never worry about chemical treatment again. However, if it does not work, cleaning and repair costs to remove corrosion and scale deposits can far outweigh potential savings.

Magnetic fields can have effects on ions and particles in solution, but translating this to corrosion and scale prevention is an example of a pseudoscientific leap of faith. This is exemplified by many different explanations of how magnetic devices condition water, and the many different designs available from different manufacturers. For example, some say that electromagnets are necessary, while some use permanent magnets. Some devices spin water as it goes though the magnet, and some must pass water over magnets at specific angles. Some say the magnetic effect "lasts for up to five days," and others indicate the water must be "retreated" on each pass through the system. The variety of explanations does not give much confidence that the true effect is known and understood.

The majority of nonchemical devices claim to prevent mineral scale, and some claim to prevent corrosion. This is certainly not true of magnetic devices, as these are proven to cause corrosion. Most do not claim to prevent biofouling and are often used with biocides. Some electrolytic devices that release copper or silver ions, which are toxic to microbial organisms, can help minimize biofouling, but devices that work by magnetic, electrostatic, or radio frequency, do not have this effect. Prevention of mineral scale is claimed to occur by modifying ions in solution, so that they are attracted to each other rather than to system piping. Other explanations are that the charge on scale particles is modified, so that amorphous particles rather than hard crystalline scale are formed. Either way, the "small, amorphous, scale particles" can supposedly be flushed from the system rather than deposited on heat exchange surfaces.

Complicating this picture is that several university studies conducted on magnetic water treatment do show that there can be a fundamental effect of magnetism on ions and particles in solution. Many of these studies appear in technical journals rather than peer-reviewed scientific journals. In many cases, experiments are not repeated or cannot be repeated (like the infamous "cold fusion" experiments in 1989). In addition, these studies of fundamental effects on ions and particles do not prove that magnetic treatment can prevent scale in cooling tower systems. Thus, any user of nonchemical devices should still monitor system performance on a regular frequency to evaluate system status.

SECTION 3.4

Applications—Water Safety for Building Water Systems

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CHAPTER 20

Legionella and Legionellosis

Most organisms that live and grow in engineered water systems do not represent a significant health hazard to humans. The previous chapter discussed the health-related risk due to *Legionella* and other opportunistic waterborne pathogens if engineered water systems are not properly managed. Of particular concern is *Legionella pneumophilia* serogroup 1, which causes over 90% of the legionellosis outbreaks that occur worldwide. Unfortunately, this potentially pathogenic pneumonia-causing bacterium can sometimes be found in engineered water systems. *Legionella pneumophilia* is a member of a genus, or group of bacteria, called *Legionella* (Fig. 20.1). Engineered water systems can become contaminated with *Legionella* because these bacteria are common in many natural waterways, like lakes and rivers. Other human-made or engineered water systems can also be contaminated by *Legionella*. For example, many types of systems including spas, decorative fountains, and even potable hot water systems may be contaminated with *Legionella*. All of these systems can provide adequate environmental conditions for these bacteria to survive and grow. *Legionella* cause a disease called legionellosis that includes both Legionnaires' disease and Pontiac fever.

The purpose of this chapter is to provide basic information on *Legionella* bacteria, the diseases caused by these bacteria, the factors that increase risk of infection from these bacteria, and sources of risk. Understanding these characteristics will help a facility or utilities manager determine the best course of action for managing risk from systems like cooling towers and potable water systems. Aspects of monitoring, assessing the risks, regulations relating to *Legionella* management, and treatment are covered in Chap. 21 on Water Management Programs for Engineered Water Systems.

Figure 20.1 *Legionella pneumophila* bacteria first isolated by Charles Shepard and Joseph McDade of the CDC in 1977. (*Courtesy of US Department of Health and Human Services, Source: National Library of Medicine, Images from History of the Public Health Service.*)

The Disease

Pneumonia is an ancient disease of the lungs that is caused by both viral and bacterial sources. *Legionella* bacteria were first identified as a cause of a pneumonia-like disease in humans in 1976. Since being discovered, *Legionella* bacteria, the systems that may harbor the bacteria, and the conditions that encourage *Legionella* growth, have been studied in great depth.

Legionellosis is the term used to describe all infections caused by *Legionella* bacteria. This includes both Legionnaires' disease and Pontiac fever (described later). Legionnaires' disease is the more serious illness. Although large outbreaks involving several hundred people have occurred, Legionnaires' disease is uncommon. This disease must be taken seriously because the consequences can be severe and the disease is deemed preventable.

The number of legionellosis cases that occur annually are difficult to determine. Even when diagnosed, the disease is sometimes not reported, so the total number of actual infections is probably higher than statistics suggest. Larger outbreaks are more commonly reported because of the publicity surrounding the disease. Sporadic cases may go unreported. The Centers for Disease Control and Prevention (CDC) states that between 8000 and 18 000 people are hospitalized in the United States each year due to legionellosis. The European Union (EU) estimates the occurrence of legionellosis varies from

120 cases per million people, depending on the reporting procedures of individual European countries. Both the CDC and EU estimate the actual number of cases to be higher because some cases are not reported. Projecting the CDC value to the world population would suggest that there might be as many as several hundred thousand cases of Legionnaires' disease each year. Most of the cases are probably sporadic, involving only a few people. About 20% of the cases are acquired during hospitalization, and 10 to 20% can be linked to larger outbreaks. The mortality rate is 5 to 20% of people who contract the disease, and the susceptibility of the individual to the disease is an important component of both contracting the disease and mortality (Bartram, et al.).

Legionnaires' Disease Symptoms

Legionnaires' disease is a serious infection of the respiratory system. Legionnaires' disease may be difficult to differentiate from other types of bacterial pneumonia because the symptoms are similar. Individuals will have high fever, chills, headache, fatigue, and muscle pain. A dry cough develops, and most patients suffer breathing difficulty. Some patients also develop diarrhea or vomiting and can become confused or delirious. The disease will develop in 2 to 10 days after exposure to the bacteria and can persist for weeks or be fatal if not treated properly. When properly diagnosed and detected early, Legionnaires' disease can be treated with antibiotics. In those people who survive a severe infection, weakness, poor memory, and fatigue, can last for months after the pneumonia symptoms are gone. Lung damage can persist for even longer periods after severe infection.

While the symptoms can be clearly described, only a qualified healthcare professional can diagnose legionellosis. Anyone with these types of symptoms should seek immediate attention by a physician.

Susceptibility

According to the CDC, most people exposed to the bacteria do not become ill. Healthy people under 20 years of age generally do not become ill, even if exposed to *Legionella pneumophila*. Healthy people over 20 years of age can catch the disease, but healthy people generally have a lower risk of death due to the disease. In most cases, only a small percentage of those exposed to the bacteria will develop disease symptoms. According to the World Health Organization (WHO), 0.1 to 5.0% of the general population may catch Legionnaires' disease if exposed to the bacteria (Bartram, et al.).

The physical condition and health of the person exposed to *Legionella* bacteria are important components of whether or not the individual develops the disease. Legionnaires' disease occurs most often in elderly people and those that have some common risk factors. The age factor varies considerably in different references from people over 40 years to people over 65 years. Examples of additional risk factors include smoking, cancer or suppressed immune system, lung or respiratory disease, chronic restrictive lung disease (like emphysema), and liver or kidney failure (Bartram, et al.) and heart disease. This is not necessarily a complete list of risk factors and only a qualified medical practitioner can properly assess the susceptibility of an individual to *Legionella* bacteria. Data from certain regions also suggests that men are more likely to contract Legionnaires' disease than women and that contracting the disease through person-to-person contact is unlikely.

Pontiac Fever Variant

Pontiac fever is a less serious infection that causes a flu-like illness. This disease is rarely fatal even though Pontiac fever is caused by *Legionella* bacteria. It is named from an outbreak that occurred in Pontiac, Michigan in 1968. The symptoms of Pontiac fever are headache, fatigue, fever, joint and muscle pain, and in some cases, nausea, vomiting, and coughing. No deaths have been attributed to Pontiac fever. This disease is often considered similar to influenza rather than pneumonia.

As opposed to Legionnaires' disease, Pontiac fever can affect healthy people and as many as 95% of exposed individuals may catch the disease. Typically, the incubation period is 13 days, and the disease lasts typically only 25 days. Treatment is generally not necessary for recovery from Pontiac fever (Bartram, et al.).

First Identified Outbreak

The first time *Legionella* was recognized as the cause of disease occurred after the convention of the American Legion in Philadelphia, Pennsylvania in 1976. Many attendees and workers at the hotel where the convention was held suffered from a serious pneumonia-like illness. Before the outbreak ended, 221 people became ill, many were hospitalized, and 34 died (Edelstein, et al.). The specific cause of the disease outbreak was not immediately identified. About six months later, scientists identified the cause to be a specific bacterium. *Legionella pneumophila* was the genus and species name given to the bacterium. The disease was called Legionnaires' disease, because of the connection to the outbreak at the American Legion convention.

A possible source of the bacteria for this outbreak was the heating, ventilation, and air-conditioning (HVAC) system in the hotel. The true source could not be identified, because the bacteria were not identified until six months after the outbreak. Those that became ill had apparently inhaled droplets of contaminated water from some part of the HVAC system. The droplets could have come from the condensate on the cooling units in the rooms or possibly drift from the cooling tower on the roof of the hotel.

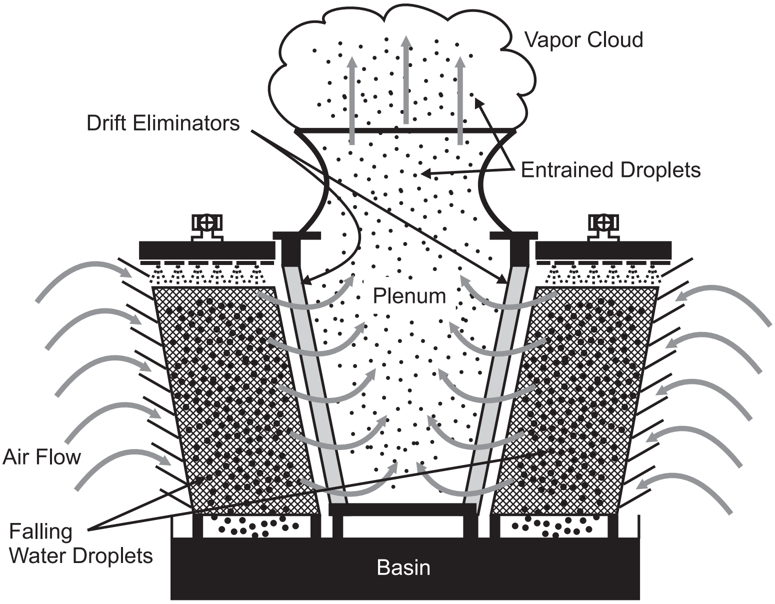


Figure 20.2 The small water droplets that escape the drift eliminators are known as drift. If *Legionella* bacteria are present in the tower water, the drift can carry the bacteria out of the cooling tower. The condensed vapor cloud from the evaporated water is not drift and does not carry the bacteria.

Drift is an aerosol of water droplets that is carried out of the cooling tower by the airflow as illustrated in Fig. 20.2. Refer to Chap. 14 on Cooling System Dynamics for more on drift. Cooling towers are designed to evaporate water for cooling. The evaporated water vapor will not carry the bacteria. Depending on the effectiveness of the drift eliminators in the tower, varying amounts of drift will be carried out of a cooling tower by the airflow. If the bacteria in the drift were carried into the person's lung by these small water droplets, the bacteria could grow and multiply in the lungs of susceptible individuals, causing the disease.

Other Outbreaks

Previously unsolved pneumonia outbreaks were studied after *Legionella pneumophila* was first identified from the Legionnaires' convention outbreak in 1976. Specimens had been saved from the 1940s through the 1960s from these unknown cases of pneumonia. Special testing showed that several of these saved cultures contained *Legionella*, and those illnesses had been Legionnaires' disease.

Since 1976, numerous sporadic cases of Legionnaires' disease have been occurring each year, with larger outbreaks involving many people occurring periodically. Outbreaks have happened in different parts of the world involving contaminated water from different types of systems, not just cooling towers. The following are examples of some outbreaks to illustrate the types of water systems that may be involved.

In 1996, about four people in two groups of tourists staying in campsites in Spain and southern France developed Legionnaires' disease. There were no cooling towers or spas at these facilities. *Legionella pneumophila* serogroup 1 was found in the hot water system of one of the shower facilities. While a clinical connection could not be established for this site as the cause, the hot water system was the most likely source of an aerosol capable of carrying *Legionella pneumophila* into a person's lungs (Infuso, A. et al.).

The Westfriese Flora (flower show) is held annually in Bovenkarspel in the northwest of the Netherlands. The show features agricultural and consumer exhibits. The February 1999 show attracted 80 000 visitors. Subsequently, 181 people who had visited during the second half of the show developed pneumonia from *Legionella*, and 21 died. A water sample from one of the whirlpool spas in the consumer products exhibits contained *Legionella pneumophila.* This water was shown to be the source of the bacteria by comparing cultures derived from the patients to cultures from the water (den Boer, J. W. et al.).

About 90 people were diagnosed with Legionnaires' disease out of about 50 000 people, who attended a trade fair in Kapellen, Belgium in November 1999. Almost all of the people who became ill required hospitalization, and five of the patients died from the disease. Testing showed that the length of time spent in particular areas in the exhibition hall was probably associated with the disease. The sources of the bacteria, found in that part of the exhibition hall, were a whirlpool and a fountain that were contaminated with *Legionella* (de Schrijver, K. et al.).

A rather unique individual case occurred in California in the 1990s where a dentist died from legionellosis. Subsequent investigations showed high levels of the same *Legionella* species in the dental unit water system at his office (Atlas, R. M., et al.).

Other large outbreaks have occurred in other places, including an outbreak at the opening of an aquarium in Melbourne, Australia in 2000. A community outbreak in Murcia, Spain in 2001 involved over 700 people who developed illness. The source was not identified, but thought to be a cooling tower near the center of town. In 2014 industrial cooling towers were thought to be linked to a significant outbreak in Portugal whilst in New York City in July of 2015 over 124 cases and 12 deaths were attributed to a cooling tower located on the roof of a hotel in the Bronx.

Thus, *Legionella* can be found in a variety of human-made water systems that use natural water sources, municipal treated drinking water, or may be contaminated with windblown dust.

The Bacteria

There are many members of the genus *Legionella*, also referred to in the plural form, *Legionellae*. *Legionellae* are rod-shaped, aerobic bacteria found widely in nature as well as in many human-made water systems (Fig. 20.3). *Legionella* can be determined by a variety of methods, including standard plating techniques and specific antibody testing. Figure 20.4 shows an example of an agar plate with *Legionella* bacteria. The genus *Legionella* has over 50 different species according to the WHO. *Legionella pneumophila* is just one of the species that is known. Twenty *Legionella* species have been reported to cause human pneumonia. The remaining 30+ species have been isolated only from water sources. All but two of the *Legionella* species that have been isolated from patients have also been found in the environment.

Legionella continue to be studied; therefore, it is likely that more species will be identified. Each *Legionella* species may be divided into different serotypes or serogroups based on the tests used to identify the bacteria. Bacteria belonging to the same serogroup exhibit a similar response to a set of antigens used in an antibody tests. *Legionella pneumophila* serogroup 1 is the organism associated with most outbreaks of Legionnaires' disease.

Species other than *Legionella pneumophila* also cause respiratory infections similar to Legionnaires' disease. The WHO estimates that approximately 70% of *Legionella* infections are caused by *Legionella*

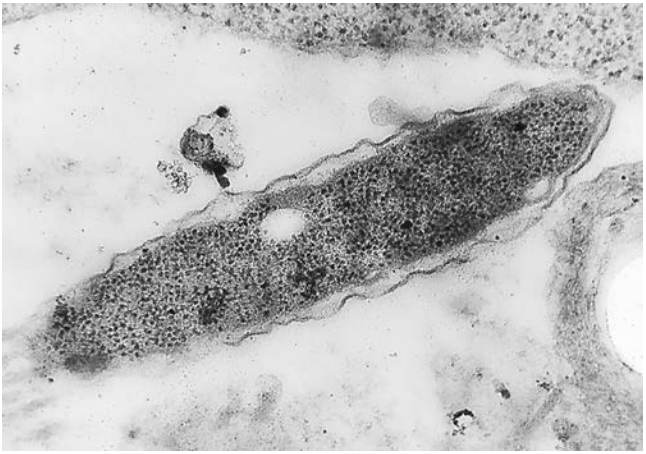


Figure 20.3 *Legionella* cells are rod-shaped bacteria as shown in this transmission electron micrograph of a *Legionella pneumophila* bacterium, magnified approximately 119 500×. (*Courtesy of CDC Public Health Image Library*.)

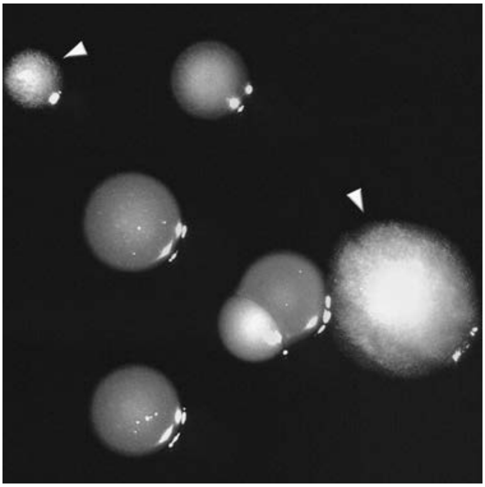


Figure 20.4 Two *Legionella pneumophila* bacterial colonies (arrowheads), among other bacterial colonies grown on buffered charcoal yeast extract agar. (*Courtesy of CDC Public Health Image Library.*)

pneumophila serogroup 1, about 20 to 30% are caused by other serogroups, and 5 to 10% are caused by non-pneumophila species. The 5 to 0% of non-pneumophila infections are based on exposure to several species, such as *Legionella micdadei*, *Legionella bozemanii*, *Legionella dumoffii*, and *Legionella longbeachae* (Bartram, et al.). In cases in Australia, the United States, and Japan, *Legionella longbeachae* has been associated with exposure to potting composts. How infection from potting compost occurs is not fully understood (Fields, et al.).

Occurrence

Legionella bacteria can be found in a wide variety of natural waters. It has been found in well water, surface water (rivers and lakes), mud, and soil samples. Even chlorinated drinking water has been found to contain the bacteria on occasion. *Legionella* are generally warm-water bacteria, and the optimum pH range for growth of *Legionella* in water is 5.5 to 8.5. These conditions are often within the range of natural and many human-made water systems.

Conditions for Growth and Proliferation

Legionella survive and grow best under specific conditions in water systems, including warm water temperature in combination with stagnant conditions, deposits, and biofilms. Stagnant conditions or water age can reduce biocide residual, reduce exposure of the organisms to the biocide, and promote deposit formation. These conditions allow complex biofilms to form and protozoa to grow.

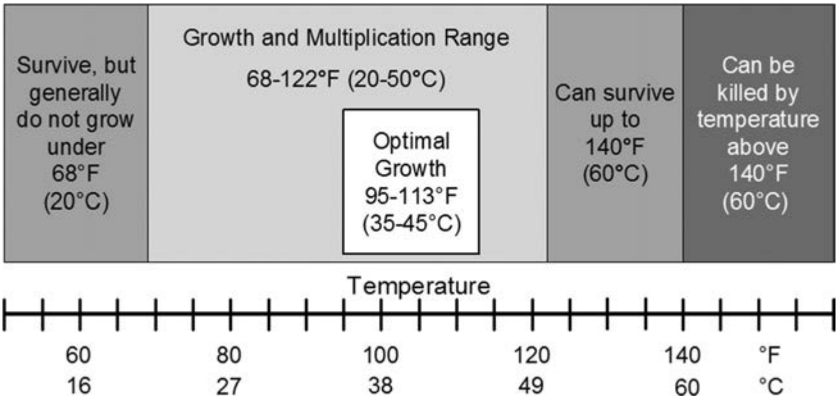


FIGURE 20.5 Illustration of the viable temperature range of *Legionella*. Sufficient contact time at temperature above 60°C (140°F) is necessary to kill the bacteria.

Water Temperature

Warm water temperature is an important factor for growth of *Legionella* bacteria. Growth and multiplication of *Legionella* can occur when the water is 20 to 50°C (68–122°F). Optimal growth occurs when the temperature range is 35 to 45°C (95–113°F). They seldom grow below 20°C (68°F) and do not survive above 60°C (140°F). They may be dormant in low-temperature water but begin to grow when the water temperature rises above 20°C (68°F). Water temperature above 60°C (140°F) can kill the bacteria, if the temperature is maintained for sufficient time in contact with the bacteria (Fig. 20.5).

Stagnant Water

System design conditions that produce stagnant water or water age can promote growth of microorganisms, since microbial control programs have reduced effectiveness in stagnant areas. Stagnant water is a health concern, if the system water is contaminated with *Legionella* bacteria. Examples include non-flowing or low-flow areas in a cooling tower basin, a water tank with low flow, or dead leg piping. These areas allow sediment, sludge, scale, iron deposits to collect and biofilms to grow. These deposits can provide a safe place for *Legionella* bacteria to grow by providing a source of inorganic and organic nutrients for bacterial growth.

However, stagnation is not the primary factor that determines if biofilm will form. Biofilms also form on surfaces with high water flow rates, such as heat exchanger tubes. Flow rate may determine the type of biofilm formation (morphology and composition). *Legionella* are aerobic bacteria; therefore, the water must contain some oxygen for these bacteria to grow. Anaerobic stagnant areas of a system may be less prone to *Legionella* growth compared to other areas that have reasonable flow rates and oxygen content (such as tower fill).

Role of Biofilms

The presence of other microbial growth, including algae or bacterial biofilms, can provide a suitable environment for growth of *Legionella* (Fields, et al.). Biofilm formation is a normal part of the life cycle of many microorganisms and occurs in both natural and human-made water systems. A biofilm is a matrix of mixed bacterial populations that adhere to each other and to solid surfaces in water. Biofilms are complex heterogeneous microbial ecosystems that may consist of many bacteria, algae, and protozoa. Generally, biofilms form on submerged surfaces in a body of water, whether natural or human-made. Biofilms can form in flowing water, in areas of low water flow, and where water is stagnant. On surfaces of human-made water systems, biofilms contain a large majority of the microbial population in the system, and only a small part of the population is floating in the bulk water. Chapter 17 on Cooling Water Biology provides more information on bacterial growth and biofilms.

Biofilms provide a habitat that allows proliferation of a wide range of microorganisms, including *Legionella*. The biofilm facilitates nutrient and gaseous exchange, and protects microorganisms not only from biocides, but also from periodic changes in physical conditions like temperature (Bartram, et al.). A biofilm can protect some of the bacterial population from biocides and attempts at physical removal, especially in areas where surfaces are scaled or corroded. The availability of complex nutrients within biofilms, has led some researchers to propose that biofilms may support the survival and multiplication of *Legionella*. In an experimental study of an ideal system, a biofilm composed of naturally occurring waterborne microorganisms, has been shown to support growth of *Legionella* within that biofilm (Rogers, et al.).

Role of Protozoa

Legionella can live inside specific amoebae and some protozoa as facultative parasites. Facultative organisms are those that are able to grow in different environmental conditions, for example, in either the presence or absence of oxygen. *Legionella* are able to infest at least 14 different species of protozoa, where *Legionella* can thrive and multiply. An example of *Legionella* growth inside of protozoa is shown in Fig. 20.6. Protozoa are important for the survival and growth of *Legionella* in both natural and human-made environments. Protozoa have been detected in systems implicated as sources of legionellosis (Kwaik, et al.).

However, not all protozoa are acceptable hosts for *Legionella* growth, indicating that a degree of host specificity may be involved.

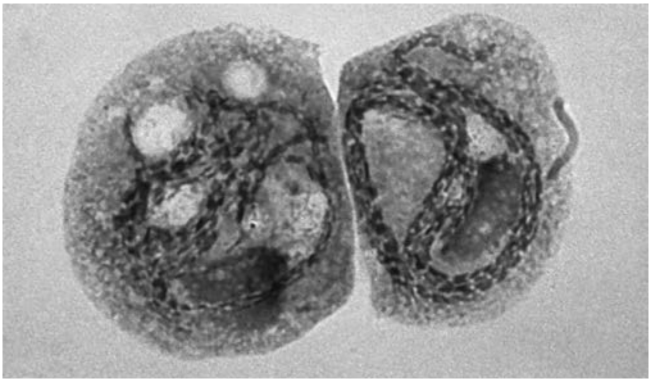


Figure 20.6 Two protozoa containing chains of intracellular *Legionella pneumophila* bacteria that are undergoing multiplication. (*Courtesy of Don Howard, CDC Public Health Image Library*.)

Only protozoa that are capable of ingesting the bacteria and forming a vacuole (like a cyst) around the bacteria will promote growth of *Legionella*. The bacteria will multiply inside the protozoa until the bacteria rupture the protozoa cell wall and are released into the surrounding water (Fig. 20.7).

Protozoa can help to protect *Legionella* from the effects of biocides and thermal disinfection. The presence of protozoa in a human-made water system indicates greater microbial diversity and suggests poor control of biological contamination. Under adverse conditions,

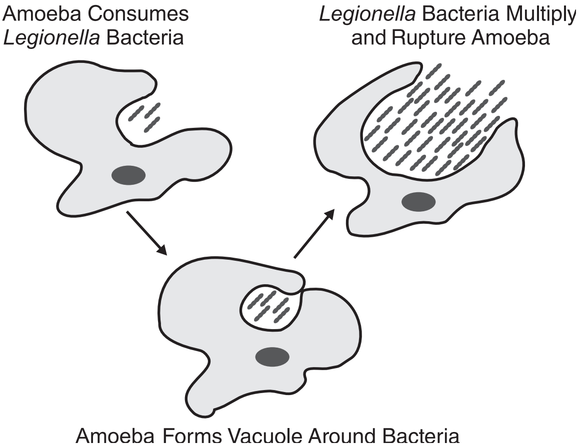


Figure 20.7 Illustration of growth and multiplication of *Legionella* bacteria inside protozoa.

certain protozoa species can form a cyst that allows them to survive through the unfavorable conditions. *Legionella* can also survive inside the cysts formed by protozoa when environmental conditions are harsh. The presence of *Legionella* within protozoan cysts can make control of *Legionella* more difficult in heavily contaminated water systems. Some researchers propose, that this mechanism, may allow *Legionella* to survive within airborne aerosols. It is now believed that adaptation to live within protozoa is what gives *Legionella* the ability to infect humans.

Operating conditions that are favorable for *Legionella* growth in a particular system may be impossible to change. However, design factors that produce stagnant conditions or allow collection of deposits may possibly be changed. Treatment to minimize biological growth in general can also help to minimize the risk from *Legionella*. See Chap. 21 on Water Management Programs for Engineered Water Systems for more details on control methods for *Legionella*.

Sources of Risk

If the water contains *Legionella* bacteria, human-made water systems that produce aerosols, mists, or sprays of fine water droplets that can be inhaled and penetrate deep into the lungs, pose the greatest risk for infection. Many different types of water systems can form aerosols and give *Legionella* the opportunity for growth. Cooling towers and evaporative condensers may be the most notorious systems, but are not the only source of legionellosis infections. Many other systems have the right characteristics and have been associated with Legionnaires' disease. Examples include:

- Whirlpool spas that aerate or rapidly agitate the water
- Hot and cold potable water systems with showerheads or other sprayers
- Spray ponds
- Humidifiers and misters
- Ornamental fountains and water features
- Supermarket vegetable misters
- Respiratory therapy equipment involving water or oxygen humidifier reservoirs
- Dental hygiene equipment water systems
- Eating ice chips (by aspiration) from contaminated ice machines

Therefore, even systems with potable water may be a source of potential infection, if the correct conditions exist and a susceptible person is nearby.

A person is not likely to get legionellosis by simply drinking water containing the bacterium, or swimming in water containing *Legionella.* The person would have to aspirate some of the water deep into the lungs for the disease to occur. Aspiration can occur when taking a breath while swimming or through improper swallowing that causes water to be drawn into the lungs. Aspiration is a documented route of infection for *Legionella* entry (Fields, et al.).

The disease is only contracted via the respiratory route, either by inhalation of contaminated aerosols or aspiration of contaminated water. Both the CDC and WHO state there is no significant evidence of transmission of either Legionnaires' disease or Pontiac fever from person-to-person contact, although one case is being investigated following to outbreak in Portugal in 2014.

Risk of Disease

The minimum concentration of bacteria in the water that causes infection is not known. A person will be infected only if the right set of conditions exists. However, the exact conditions under which an infection will occur are unclear. For example, if too few *Legionella* are present in an aerosol particle, if there are insufficient numbers of *Legionella*-containing aerosol droplets, or if the type of *Legionella* in the particle is not capable of causing disease (not virulent), then legionellosis infection of a susceptible person may not result.

The following three risk factors as illustrated in Fig. 20.8 must exist for Legionnaires' disease to be contracted by an individual:

1. Favorable conditions for growth and multiplication (amplification) of the organism. Warm, oxygenated water, within 20 to 50°C (68–122°F), and the presence of deposits containing rust (iron), scale, or other microorganisms.
2. An aerosol of fine water droplets containing *Legionella* must be formed and aspiration of contaminated water must occur. The only exposure route for *Legionella* is inhalation or aspiration of water droplets containing the organism.
3. The aerosol or water droplets containing the infectious *Legionella* cells must enter the lung of a susceptible individual. Populations most at risk for Legionnaires' disease include, but are not limited to, the elderly, individuals with suppressed immune system, and individuals with pulmonary or liver dysfunction. However, even people with no previously indicated health risks have contracted Legionnaires' disease.

Therefore, determining whether a specific water system could cause an outbreak of legionellosis requires an assessment of risk, and is not a simple "yes" or "no" answer. The disease may not result when someone is merely exposed to water containing *Legionella* because the

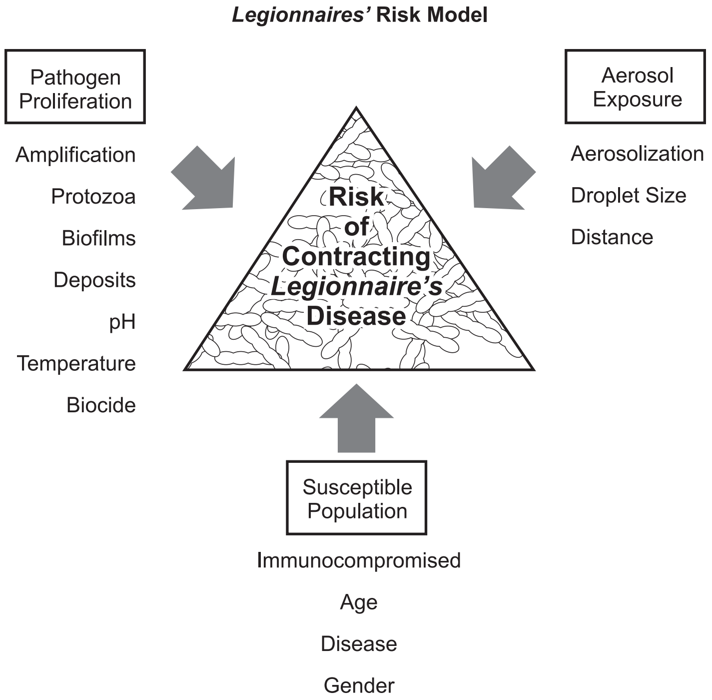


FIGURE 20.8 Illustration of the three risk factors that must combine in order for Legionnaires' disease to occur in an individual.

other risk factors are absent. Similarly, the presence or absence of *Legionella* bacteria in a water sample is not a measure of risk. *Legionella* may be present in a water system but not detected in the tested sample of water for a variety of reasons. Chapter 21 on Water Management Programs for Engineered Water Systems covers the aspects of detection, risk management, and water treatment protocols in more depth.

CHAPTER 21

Water Management Programs for Engineered Water Systems

Engineered or building water systems such as centralized cold and hot potable building water systems and nonpotable building water systems can become colonized with *Legionella* and other opportunistic waterborne pathogens and can present a significant risk to infection in human-occupied buildings. At-risk buildings can include commercial, institutional, multi-unit-residential, and industrial buildings, including, but not limited to, hotels, office buildings, hospitals, and other health care facilities, assisted living facilities, schools, universities, commercial buildings, industrial buildings, and centralized systems in multifamily residential buildings. Buildings with noncentralized building water systems and single-family residential buildings can also be at risk.

Traditionally, the water treatment industry has reviewed operation of engineered water systems purely from the perspective of plant efficiency or an operational performance goal. Consideration has focused on reducing potential for scale formation, minimizing corrosion, and preventing microbiological proliferation. Poor control of these parameters causes loss of system efficiency and increased operational costs. These elements are still key performance indicators, but as identified in previous chapters, there is an increasing concern on a global scale over waterborne disease associated with *Legionella* and other waterborne pathogens that may reside within an engineered water system. Now, in addition to traditional water treatment considerations for cooling systems or the general operation and maintenance of potable water systems, the owner of the legal responsibility for the site is required to manage exposure risk of workers and members of the public to such organisms. In some countries, the need for this consideration is a statutory requirement. In the absence of such regulatory enforcement, control of *Legionella* is still deemed a "duty of care" responsibility.

With respect to maintaining hygiene and reducing risk within the engineered water system, a sound knowledge of the ecology of the microorganism in question is required, along with expertise to translate this knowledge into good working practice. This requires a special skill set to those employed for traditional operational management of engineered water systems and necessitates an understanding of water safety to be able to (1) assess the risks, (2) determine the best strategy to reduce risk, and (3) understand the requirements for proactively managing risk to a health-based goal within the context of a written Water Management Program, Water Safety Plan or Risk Assessment (collectively, the "*Program*").

Acknowledging the fact that the number of cases of legionellosis has historically been under-recognized, under-diagnosed, and under-reported, the actual number of people diagnosed with Legionnaires' disease has increased significantly over the years and outbreaks have occurred in many geographical regions of the world. This may be attributed to a number of factors such as differences between surveillance systems used in individual countries and aging population and infrastructure. In order to align surveillance methodology and monitor cases of legionellosis, many countries within Europe have contributed to an international surveillance program (European Legionnaires' disease Surveillance Network—Eldsnet). In the United States, outbreaks are typically reported by local state or city health agencies to the Centers for Disease Control and Prevention (CDC).

Collated results from global surveillance data indicate outbreaks of legionellosis have been associated with several different types of systems, including cooling systems and hot and cold potable water services such as those provided within buildings. In response to worldwide concern over water safety and implications of creating risk to health, various management programs have been specifically designed to assist the owner of engineered water systems, to reduce the risk of exposure to *Legionella*, and meet regulatory requirements of countries in which they operate. Although it can be concluded that the terminology may differ within some of the control programs used globally, there are basic components of risk management and keeping the water systems safe that are common to all processes.

For example, it is recognized that a nominated manager who may lead a team (water safety group or program team) would be overall responsible for identifying any water containing systems where *Legionella* may be present, and where operation of those systems may create an aerosol, which could be inhaled. The manager (with assistance from colleagues) is then required to prepare a risk statement and provide a suitable *Program* to control risk. Working knowledge of such systems and implementation of specific water safety programs is an important management strategy for reducing risk of exposure to these bacteria. This is in accordance with both legislative and good practice standards requirements of many countries and is deemed best practice.

This chapter has been compiled in order to provide an understanding of the manager's role to comply with global legislative and best practice requirements to control and limit exposure to *Legionella* bacterium (and by default other opportunistic pathogens) that may be associated with engineered water systems.

Managing the Risk: Regulatory Position and Global Guidance

Sporadic outbreaks of legionellosis continue to occur. One typical response to such an event at a national level may be to review and possibly revise current statutory guidance. In some countries, general health and safety regulations may not specifically mention *Legionella*, but may have generalized references to the protection of personnel within the working environment from biological agents or environmental hazards. Fortunately, several countries have realized that exposure to *Legionella* is preventable, but only if health-related risks are assessed and preventative practices are implemented and monitored.

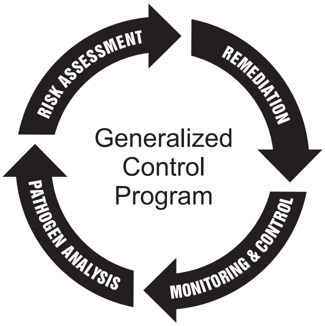
As a consequence, several countries have introduced regulatory instruments, which require senior management or those responsible, for an industrial plant, large commercial buildings, hospitals, or managing government owned buildings, which may be frequented by the general public or employees, to consider whether there is a foreseeable risk of exposure to *Legionella*, and whether sufficient emphasis has been placed on reducing that risk.

Such guidance now exists and is practiced in many countries, for example, the United Kingdom, France, the Netherlands, Australia, Spain, Germany, and Italy. In the United States, the American Society of Heating, Refrigerating and Air-Conditioning Engineers (ASHRAE) produced ANSI/ASHRAE Standard 188 entitled "Legionellosis: Risk Management for Building Water Standards," as a practice standard for managing risk, which is gaining acceptance and has been codified by the state of New York and the city of New York as a requirement for managing risk in cooling water systems. In the event of an outbreak of legionellosis or failure to satisfy local government inspection, senior management responsible for control procedures will likely be investigated, in order to determine whether there has been a breach of any legal duty, with the threat of financial or imprisonment penalties as a consequence of a work-related death associated with their premises. In the United States, the Occupational Safety and Health Administration (OSHA) has authority under the General Duty clause, to issue fines and citations if facilities are found to be negligent. From an international perspective, the World Health Organization (WHO) has recognized the concern of possible exposure to *Legionella*, and in 2008 released a publication entitled "*Legionella* and the Prevention of Legionellosis," which reviews general epidemiological aspects and approaches to risk management. In 2011, the WHO also released documentation relating to water safety in buildings.

All this available information can be used by individual or corporate organizations, to prepare a site-specific *Program*. In general, similar recommendations are identified within all previously mentioned guidance, and a *Program* may be generalized into the following process (Fig. 21.1):

1. Establish a *Program team* who owns the responsibility for the development, implementation and management of the *Program*. The team should appoint a responsible person or duty holder.
2. Describe *building water systems* with text and simple flow diagrams or schematics.
3. Assess *building water systems* to determine where *Legionella* could grow, where sources of aerosols can occur and the risk of human exposure. Goal is to assess and prioritize risk.
4. Define where *control measures* should be applied (plus applicable control limits) and how to monitor them. Goal is to identify needs for safe operation including system maintenance, regular examination or inspection, and system testing and monitoring.

FIGURE 21.1 Elements of a water management program.



5. Establish procedures for *corrective action* when control limits are not met. This includes provisions for instruction and training plus escalation and incident response plans.
6. Confirm the *Program* is working as designed and it is effective on a regular basis (i.e., quarterly). Goal is to validate the *Program* when implemented as designed, effectively control the hazardous conditions throughout the building water systems, and the goal is to verify the *Program* is being implemented as designed.
7. Document and communicate all activities.

General Management Considerations

Failing to employ preventative control programs can carry severe consequences such as sickness and fatalities that can be associated with an outbreak of legionellosis. Numerous financial penalties can affect the incumbent company, for example, adverse media exposure, share price fall, or brand damage. In some countries, a charge of breach of health and safety guidance may reside on government websites that are open to the public domain. Business associates, both future and present, may view this information.

The information provided below identifies the need to introduce various management processes and discusses the requirement to determine individual responsibilities of all personnel involved with a *Program*.

Generally, health and safety responsibilities for an individual site cannot be transferred to third parties, such as companies offering services to assist compliance. However, service company personnel may be invited to participate on the *Program team*. It is important, therefore, that the responsible manager ensures that the services provided actually satisfy the need of the site, and that they form an effective part of the *Program*. It is equally important that clear lines of responsibility and communication are identified between the client and service provider. It is acknowledged that inadequate management, lack of training, and poor communication have all been associated with outbreaks of Legionnaires' disease, which emphasizes on the importance of effective management of the *Program*. Such comments are borne from the experience of previous outbreaks, where the consequences of mismanagement have resulted in personal injury or death, and have become critical key learning points.

It is vitally important that all individuals involved in the risk management process, which includes company senior management or owners, engineers, health and safety representatives, and associated service providers, understand their individual roles and responsibilities in relation to reducing the risk of exposure to the *Legionella* bacterium. Ideally, right from the start of any contractual agreement, it should be defined by individual, who will do what, where and when. Training will need to be undertaken to correspond to the level of responsibility accepted.

Assessment of Risk

The most logical starting point when considering a *Program* is to determine whether an inherent risk actually exists in relation to the specific hazard being considered. In most global *Legionella* control guidelines, the initial phases of a control program involve undertaking assessment of whether a risk actually prevails and where it is reasonably likely to occur. Use of such terminology as risk assessment may differ from one guidance to another, but there is generalized acceptance of establishing a baseline of risk that is common to many health and safety practices.

The complexity of assessing risk has in some instances, led facility owners and managers to delay establishing a *Program*. However, practical experience and observation suggest that prioritizing risk assessment and developing a site specific *Program* to mitigate the risk of legionellosis is both prudent and justified. Since facility managers hold great responsibility and play a number of different roles, they cannot be expected to be experts in all areas. For specialized assessments such as *Legionella*, it is not unusual for companies to utilize external service providers to provide competent trained risk assessors or subject matter experts. Alternatively, a person or nominated team with detailed understanding of the system and risk factors, must undertake the assessment to characterize the risk.

Health and safety professionals recognize the risk assessment process, as a natural beginning to laying a foundation for the ongoing *Program*. Assessment requires being “suitable and sufficient;” in other words, it should consider all aspects of *Legionella* control and how mechanical, operational, and control procedures all interrelate. Since this bacterium has been isolated from drinking water in low numbers, even systems utilizing potable water need to be assessed. Consequently, cooling systems, whirlpool spas, hot and cold potable water systems, ornamental fountains and water features and other water systems that have the potential to release contaminated water mists have all been identified as “at risk” systems. Sites previously described earlier that contain such water systems or utilities have all been identified as sources of outbreaks, which when analyzed retrospectively, could have been prevented. Most global *Legionella* guidance views legionellosis as a preventable disease.

In relation to content, the risk assessment should be sufficiently detailed to identify and assess risk of legionellosis from all work activities and water sources on site, and to describe necessary precautionary measures needed. Each system assessment should include a process to identify and evaluate potential sources of risk, particular means by which exposure to *Legionella* bacteria is to be prevented, and means by which risk from exposure to *Legionella* bacteria is to be controlled, if prevention is not reasonably practicable. Such studies should consider all mechanical, operational, and management aspects and how these factors can be interrelated to decrease risk potential. As mentioned, if the risk assessment identifies significant risk that cannot be eliminated, the responsible manager should implement an appropriate control scheme.

A *Program* is developed using a standardized model to identify potential hazards and control measures. Risk of legionellosis is a function of many factors that can be grouped into three categories:

1. Growth Risk—the likelihood of microbial growth in the water system
2. Aerosol Risk—the likelihood of the release of aerosols or water mists from the water system
3. Human Risk—the likelihood of having susceptible people present who may come in contact with contaminated water mists

The risk of harm is a function of these factors that combine to form the causative chain, which in severe cases, can lead to infection. Each category is further discussed within the context of assessing risk potential that may be associated with an engineered water system.

Growth Risk

With respect to proliferation potential, the following need to be considered on each individual part of a system:

- Water temperature
- Deposits
- Presence of other organisms
- Low-flow areas

Water Temperature

Temperature is an important factor in keeping the *Legionella* bacterium active, since as temperature increases the normal biochemical reactions inside the cell also increase. This bacterium has an ideal growth temperature of about 37°C (99°F), but temperatures in the range of 25 to 42°C (77–108°F) can provide an ideal growth environment for *Legionella*. The general growth range is 20 to 50°C (68–122°F). When considering different water systems, the ideal situation would be to avoid temperatures in the growth range (see Table 21.1); the

Temperature	Associated *Legionella* Response
25–50°C (77–122°F)	*Legionella* amplify in this range
25°C (77°F) and below	*Legionella* survive but do not amplify
25–30°C (77–86°F)	*Legionella* amplify slowly
30–42°C (86–108°F)	*Legionella* amplify rapidly
42–50° (108–122°F)	*Legionella* amplify slowly
50–55°C (122–131°F)	*Legionella* amplify very slowly
55°C (131°F)	*Legionella* die slowly (5–6 hours)
60°C (140°F)	*Legionella* die (within 32 minutes)
66°C (151°F)	*Legionella* die rapidly (within 2 minutes)
70°C (158°F) and above	*Legionella* die immediately

Table 21.1 Temperature Effects on Survival and Amplification of Laboratory Strains of *Legionella* (US-CDC)

reasoning to keep hot water hot and cold water cold. If a cooling system is present, using temperature to control growth is not a feasible option, and additional control strategies are needed.

Hot water should be stored at 60°C (140°F), and hot water should be at or above 124°F (51°C) everywhere throughout the system to the point-of-use. In addition, the hot water return from the point-of-use should be consistently above 122°F (50°C), unless other, compensating control measures are used. Appropriate scald controls may be necessary to achieve the desired hot water temperature.

Cold water should be stored at less than 20°C (68°F), and in general, cold water should be distributed and delivered at temperature below 25°C (77°F), if practical. (Note: lower temperatures may be required by some guidance documents) If cold water temperature exceed 25°C (77°F) in any part of the system, there is greater potential for amplification of *Legionella*. At water temperature above 30°C (86°F) the potential for amplification of *Legionella* increases significantly. When water supplied to the building is near or above 25°C (77°F) and when environmental conditions, building water system design or operating conditions result in cold water temperature above 25°C (77°F) in any part of the system, other physical or chemical control measures should be considered for *Legionella* control.

Deposits

The presence of sediment, sludge, scale, and corrosion product has been identified as a source of inorganic and organic nutrients. In general, systems should be kept as clean as possible. This does not just apply to cooling towers. General cleanliness of the system is a paramount control factor in all systems and in particular for those containing large amounts of piping, which provides a large surface area. Microbiological activity can potentially migrate to such surfaces. In a similar way, the bathing load of whirlpool spas should identify the frequency for thorough cleaning to reduce risk to bathers.

Presence of Other Organisms

Legionella are often found within more dynamic environments associated with biofilms and higher life forms (amoeba). Biofilm generation is a normal part of the life cycle of most microorganisms. A biofilm is defined as a matrix of bacterial populations that are adherent to each other and to surfaces or interfaces. Biofilm provides a habitat that allows proliferation of a wide range of microorganisms, including *Legionella* although *Legionella* does not form biofilm, but rather is a "squatter" within biofilm where there is a favorable growth environment. In engineered water systems, over 90% of the microbial population is present on surfaces and in aggregates, not in bulk water (Figs. 21.2 and 21.3). Since *Legionella* are thought to be vulnerable organisms, they prefer to hide out and proliferate within biofilms, where they are protected and can even gain nutritional advantage.

Amoebae have been isolated from various water systems. These organisms can become infected with *Legionella*, suggesting that amoebae are a reservoir for these bacteria.

These biological principles obviously enable the organism to survive and reproduce, and this level of contamination may be directly linked to available food source or absence of suitable control factors. Therefore, unexpected or even predictable contamination of a cooling

Figure 21.2 Biofilm in tower fill.

FIGURE 21.3 Severe biofilm on the underside of tower fill.

system with process materials (hydrocarbons, sugars, etc.), may provide ideal growth conditions at normal operating temperature. Such contamination may overwhelm the current treatment program, making it ineffective and rendering the system vulnerable. Maintaining cleanliness in water systems is of paramount importance for controlling microbiological activity.

Low-Flow Areas

Water stagnation or water age encourages biological growth and has been implicated as a source of contamination in previous outbreaks of legionellosis. Dead legs and slow water turnover areas are prone to supporting growth. Such areas may include:

- Low flow zones of heat exchangers, where temperature and buildup of deposits particularly favor proliferation of microorganisms
- Blocked areas of cooling tower fill, where no biocidal treatment might penetrate
- Water tanks serving domestic systems that have a low water turnover rate

Piping containing water that is exposed to heat gain may be considered a dead leg area. Buildings or factories that are fed directly by water mains and do not have tanked water storage systems can create a risk. In some cases, the control program involves flushing of these little used or low-flow areas.

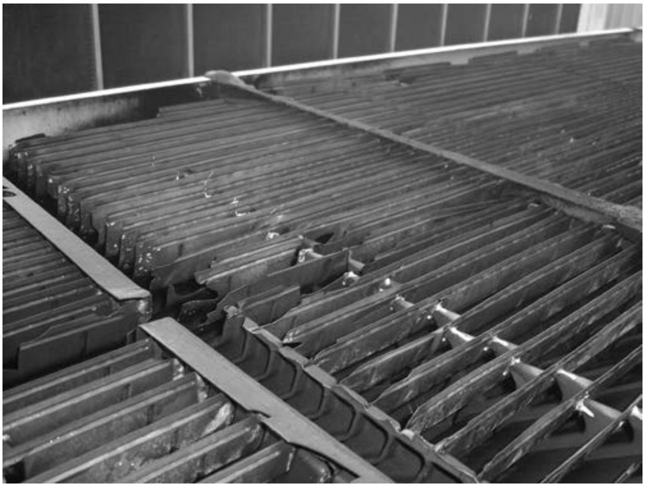


Figure 21.4 Damaged drift eliminators are a potential problem for aerosol release.

Aerosol Risk

Since legionellosis is contracted through inhalation of a contaminated aerosol (water mists), any engineered system that might create an aerosol (Figs. 21.4 and 21.5) as part of its operation needs to be considered in relation to risk potential. Should an aerosol be produced by a system that is operating at a temperature to allow *Legionella* proliferation, and where conditions provide support via nutrients, pH, and questionable cleanliness, such a system may be breaching health and safety guidance in several countries. More importantly, such a system may provide a source of *Legionella* that might infect the final link in this causative chain—the susceptible individual.

Risk assessment should identify sources of risk and suggest remedial action for implementation as part of a corrective action plan. Underlying all the mechanical, operational, and chemical aspects of

Figure 21.5 Poor control of aerosol release from a cooling tower.

the control plan is still management of the process. Without proactive management to ensure the control plan is implemented and maintained, even the best risk assessment available is likely to fail.

Human Risk

It is generally accepted that certain individuals are more susceptible to legionellosis than others. Individuals likely to be infected are males, generally over 40 to 65 years old (varies depending on the reference), or those with underlying disease like diabetes, heart disease, or those on immunosuppressant drugs. Heavy smokers and those suffering alcohol abuse are also deemed susceptible.

Manage the Risk: Water Management Program

A site specific *Program* (aka, control programs, control scheme, and water safety plans) is necessary to manage risk. It is essential to the control scheme defined in the *Program*, that any remedial work identified by the risk assessment should be implemented, and consideration given to conditions that inhibit *Legionella* proliferation and dispersion of an aerosol. It is important to note that a system risk may change during the cycle of its operation. For example, an intermittently used cooling tower may provide little risk from exposure to *Legionella*, but while offline, microbiological activity that has developed during the idle time, can seed the system once it is brought back into service. Such systems need to be cleaned and treated correctly to minimize any inherent risk. Hence, many consider intermittently used cooling towers as a major risk.

Where the risk assessment identifies a reasonably likely risk, management must initially consider whether the particular system can be removed and replaced by a lower risk system. It is considered good practice to demonstrate these considerations have been undertaken. If elimination is not practicable, it is the responsibility of the site to ensure a scheme for controlling risk from exposure, is prepared and properly implemented and managed. This scheme should include, but is not limited to:

- Up-to-date schematic diagram
- Description of correct and safe system operation
- Precautions to be taken and associated checks that ensure efficacy of the control scheme
- Remedial actions should the scheme be ineffective

Water Management Program for Cooling Systems

In the example of cooling systems, the water treatment program is a major part of the *Program* for reducing risk. This is obviously in addition to any mechanical or operational remedial actions suggested to reduce risk potential. The latter may include replacement of damaged drift eliminators, installation of aerosol reduction equipment, or even removal of outlets that are infrequently used and thereby create a possible contaminant source to the rest of the system.

Cleaning and Disinfection Programs for Cooling Systems

Failure to maintain cleanliness of the system and the water in it has been associated with several outbreaks of legionellosis. Most global guidance documentation identifies that cleaning and disinfection techniques are an important part of overall *Legionella* control strategy. Routine mechanical cleaning and disinfection of the cooling tower should be conducted in accordance with local guidance, or when the system is deemed dirty by either visual or operational factors (e.g., loss of cooling).

It is important to note that often a cursory visual inspection may give the false impression that tower packing is clean, but upon removal, deposition is often found in lower layers of the packing. Experience has shown that application of chemical cleaning procedures alone is often less effective than undertaking a chemical and manual cleaning.

The risk assessment and condition of the system dictate the specific cleaning frequency; although historically, there are periods when systems may be at higher risk. Particular care should be taken in the following situations:

- When either commissioning or decommissioning a cooling system
- In the event of major modifications to the system
- After a period of being out of service in excess of one month
- Where results indicate loss of control
- Following a suspected outbreak of legionellosis
- Where determined by local guidance for a particular industry (e.g., health care)

The method of cleaning should be selected after review of system conditions, the risk assessment, and previous history of the system. For example, in cases where heavy scaling is present, specific cleaning programs or replacement of tower fill is required. Therefore, the cleaning program may be site specific and require external expertise provided by the service provider. Best practice adopted by several countries includes addition of sodium hypochlorite (bleach) to achieve a free residual chlorine level of 5 mg/L, maintained for 5 or 6 hours (depending on local requirements) pre- and postphysical cleaning. Alternative programs, as identified in local guidance, can be implemented.

In-situ or in-place cleaning techniques may be considered if tower internals cannot be accessed. However, whichever cleaning protocol is used, it is important that the time taken to undertake such cleaning is fully scheduled into the cleaning program and that process is not compromised in any way. Incomplete cleaning and disinfection programs because of production pressures constitute a noncompliance in many countries. Supplementary control procedures such as increased monitoring or additional chemical treatments are then required.

In making a decision on the cleaning program, consideration should be given specifically to the cleanliness of the tower fill. If dirty, the fill should be removed and physically cleaned or replaced. In countries where fill removal is a legislative requirement (unless proof is available to demonstrate cleanliness), the statutory duty holder for the site must be made aware of this obligation. Techniques such as employing borescopes may be considered as additional evidence of cleanliness.

For systems that are continuously operated and cannot be shut down for cleaning, like those associated with heavy industry and large power stations, online disinfection (also known as super chlorination) should be carried out every three months or when results indicate a lack of control. This chlorination (to include addition of a dispersant) typically involves dosing the system to achieve 5 mg/L free residual oxidant for 5 or 6 hours, depending on local requirements. It is good practice to visually inspect all cooling towers if the system becomes available and if required, clean all accessible areas. In such systems, application of automated dosing and monitoring programs is often favored. Since physical cleaning is often not an option apart from periods of plant closure, the objective is to address the balance of risk by applying additional control factors. These supplementary control factors require proof of being effective, and one common approach is to increase monitoring of the system key performance indicators and to continuously apply biocide treatment.

Review of Control Measures for Cooling Systems

So how do we prove that the proactive management has been effective? Obviously monitoring the system closely helps determine whether the employed control and risk reduction procedures have achieved the objective. Monitoring programs should be devised to ensure the treatment regime and all other aspects of the control program continue to reduce risk and control can be demonstrated. When situations arise where control limits are not met, a defined management process should be followed to firstly undertake any remedial action necessary; prove that the action taken has been effective in reducing any incumbent risk; and finally ensure the event is documented. In some countries, this is called a defect/action log or escalation process. This log details all personnel held responsible for undertaking a specific action in order to return the system to a steady state and all correspondence between personnel. Such systems should be auditable, and the review process should validate and verify that the *Program* has been effective. Typical tests to include are:

- Checking system pH
- Enumeration of general bacterial levels, using for example, dip slides

- Analysis of free halogen residual
- Conductivity measurements

Such tests should be carried out on a regular basis, at least weekly or as defined by local guidance and form part of a management program. Agreement as to whether site personnel or the service provider conducts these analyses needs to be defined in the commercial contract. Free residual halogen should ideally be recorded on a daily basis, or a system to measure automatically would be deemed good practice and provide enhanced monitoring. All results must be recorded in site documentation and be available for inspection by the service company, or if the market place is legislated, by the regulating authority. Arrangements should be made for regular review meetings (recommend at least once per year minimum) in order to discuss the various control parameters, and ensure good communication by all parties concerned in the risk management. These meeting should determine the overall effectiveness of the control program.

For each of the tests above, it is important to both define the specific test methodology to use, to identify specific control parameters and to calibrate monitoring equipment at predefined intervals.

In addition to any chemical or microbiological testing, daily physical inspection of functionality of dosing equipment, cleanliness of system, chemical drum levels, etc. is considered good practice. Any comments from such a review should be recorded. Calibration of equipment should be conducted periodically in accordance with manufacturer's recommendations. Daily inspections are often the responsibility of site personnel and must be identified under designation of responsibilities within the control plan. Site personnel must therefore, be trained and competent to interpret results, take appropriate action, and communicate such details to the service provider. Accessible areas of the system should be inspected for damage or signs of contamination during daily inspections.

Arrangements should be made for dosing, testing, draining, and isolation during idle operational periods, with subsequent cleaning and disinfection. If the system is out of use for periods of longer than one week, arrangements must be made to dose the system with biocide immediately on reuse. If the cooling system is left idle for longer periods, especially during warm periods, the system should ideally be cleaned and disinfected.

Sampling and testing for the presence of *Legionella* is a useful addition to the monitoring program. Samples should be taken at least quarterly, although in some cases law may require a higher frequency. Additionally, specific conditions might arise where additional testing to those deemed routine would be important. Sampling frequency and protocol should be agreed upon between the site owner and service provider, and written into a formal service agreement, such that both parties know and understand the logic behind any intended sampling program. More frequent *Legionella* testing is required when determining efficacy of a new program or where problems have been experienced with the existing control program. If deviation from the standard control programs occurs, additional testing is required as evidence-based practice to prove that excursions in the risk management have been rectified. For example, lack of delivery of biocide due to air binding of a dosing pump increases risk potential, and additional testing may be necessary to prove continued control. Reasons for additional testing should be documented in the site file.

Heterotrophic aerobic bacteria dip slides are a simple technique for determining general bacterial activity of water samples although it is acknowledged that in certain countries use of dip slides is limited by regulations. The testing protocol for dip slides should ideally be on file such that the procedure for testing can be referenced when audited. Tests involving the use of adenosine triphosphate (ATP) may be considered to supplement the control program. Any deviation from the trend may indicate an increase in microbial activity and risk and warrants investigation. It could mean simply that a biocide product drum has emptied or that the system has suffered process contamination. In addition, for due diligence, if site personnel undertake dip slide testing, the service provider should review the testing protocol to ensure good practice.

Control Scheme for Hot and Cold Potable Water Systems

Hot and cold potable water systems in buildings can create a risk from legionellosis if poorly managed. Many individual cases of infection have been associated with such systems. Many of the control factors associated with cooling systems play a part in reducing risk from these systems. However, in most cases, water supplied to the utility is usually of potable water quality, and the level of *Legionella* contamination is expected to be at a very low level. Risk of legionellosis occurring from hot and cold potable water systems is amplified by failures in design and operation. One example being that some systems may have water feeding directly to an outlet, where others take water and store it in tanks before distribution. The use of water storage tanks may be limited by local regulations. Many health authorities implement *Legionella* control policies in recognition of them having a highly susceptible population, and that any water utility may pose risk to health. For such systems, the main risk reduction program employed by many countries is control by temperature, following a simple rule of “keep hot water hot and cold water cold.” Proof is required to ensure that this simple control process remains active. In some large sprawling distribution systems within complex buildings, attaining desired temperatures is sometimes impractical without significant capital investment. In such situations, a secondary disinfectant may be applied. Whichever control method is employed; risk assessment is still the initial starting point for a *Program*. The following points are generalized in relation to reducing microbiological activity, including *Legionella*.

System Design Factors

Distribution systems taking water from the source of entry to a building or factory, to a particular outlet, need to be installed by competent people who use only approved fittings and materials. Incorrect materials might not only contravene local standards in relation to water supply regulations, but may also provide suitable habitat for microbiological activity. In a potable water system, extensive piping and tanks (Fig. 21.6) provide a large surface area on which to deposit, and if organisms are provided with a suitable food source and temperature, biofilm formation can easily occur. Reference should be made

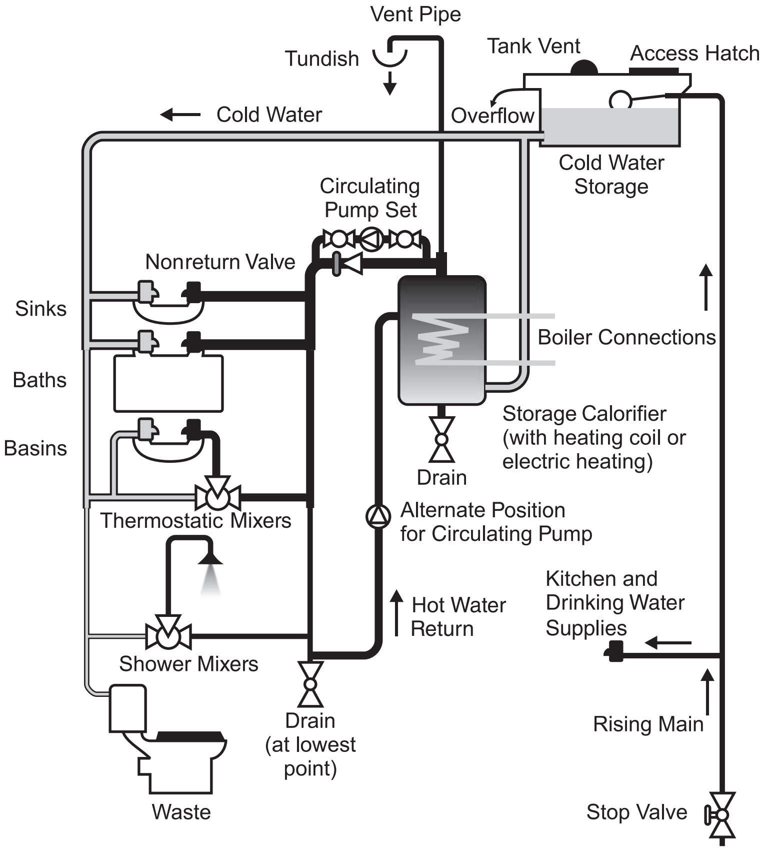


FIGURE 21.6 Example of water distribution system featuring a storage tank.

to local standards, as certain materials have been identified as supporting microbiological growth (e.g., rubber sleeves within certain flexible fittings).

Water entering an industrial or institutional site is frequently stored in a tank, which can be a source of contamination, especially if tanks and other parts of the distribution system are not enclosed to prevent entry of foreign matter. Water supply tanks should be constructed of materials that allow for cleaning and should be readily accessible for inspection and testing.

Use of multilinked storage tanks should be avoided if possible, and tanks should not allow water to stagnate. Tanks should be sized according to water usage. In general, a 24-hour maximum storage capacity is recommended, and storage time should be assessed. Occasions have occurred where hotel water storage has been designed to supply water at peak times (morning and early evening time due to shower use by guests), but operationally, the hotel may experience periods of low occupancy. During these times, water has remained in tanks for long periods and promoted *Legionella* proliferation.

As temperature is an integral factor in promoting microbiological activity, cold water supply tanks and piping should be installed such that heat gain is minimized (e.g., do not position close to a heat source, avoid solar gain, and ensure effective insulation). Since it is well documented that dead legs or low flow zones can create a suitable habitat for *Legionella* to proliferate, all such areas within the system should be avoided and those identified removed from the system.

For hot water systems, water heaters bring several engineering issues that have been related to enhanced risk. In a similar way to storage tanks, water heaters should be sized appropriately to meet demand, and be capable of heating contents to the desired temperature throughout. Since this type of equipment is prone to thermal stratification where cooler water tends to be found at the base of the unit, it is recommended that these areas of lower temperature, which are more likely to support the growth of *Legionella*, be avoided or prevented.

Like considerations made to cooling systems, hot and cold potable water systems should be maintained in hygienic condition, free from corrosion debris, scale, and biomass. Water heaters can become scaled and contaminated with debris, and they should be readily accessible for cleaning and inspection. Any debris in the base of the heater should be purged to a suitable drain on an annual basis. Alternatively, point-of-use water heaters with minimal storage and low temperature feed water should be considered as low risk and replacements for water heaters.

If fitted, accumulators should have diaphragms, which are accessible for cleaning since diaphragms have been associated with supporting bacterial growth.

The risk assessment should identify all parts of the system that present a risk. If the risk cannot be eliminated, then a control program is required.

Operational Considerations

The general growth range for *Legionella* is 20 to 50°C (68–122°F). Temperatures in the range of 25 to 42°C (77–108°F) can provide an ideal growth environment, and these temperatures should be avoided, as far as possible, within the hot and cold potable water distribution systems. Climatic conditions may result in water temperature increase, and this effect needs to be considered. To attain hot water with a reduced risk of *Legionella* contamination, water heaters with storage tanks should operate above 60°C (140°F), with hot water distribution giving a temperature of 51°C (124°F) to the point-of-use or tap. Storage capacity and rate of recovery of the water heater should be selected to meet normal fluctuations in demand. Should monitoring identify that high temperatures cannot be maintained due to operating peculiarities or design, then chemical disinfection should be considered as a remedial action.

If a water heater or any substantial part of the system is on stand-by, the water heater and recirculating water temperature should be raised to 60°C (140°F) for at least 1 hour, to reduce the risk of bacterial contamination of the system. This is a form of pasteurization for the water heater. During this period, each outlet should be flushed for five minutes. This technique is known as thermal disinfection.

Cold water supply tanks and cold water services should be maintained at temperatures below 20°C (68°F), where practicable. Hot and cold water pipes should be insulated as needed, but consideration not to insulate piping should be given if insulating piping increases risk of holding water temperatures in the growth range during long holding periods or periods of no water usage. To ensure that cold water remains cold, temperature of the incoming water should be checked at six-month intervals, such that one reading is taken in the winter months and one reading is taken in the summer. Similarly, temperature of the bulk water in the tank should be taken semiannually. Results should be recorded and action taken if temperatures show a marked increase from the norm. Ideally, temperatures below 20°C (68°F) are most suitable to restrict bacterial activity, but in some countries, incoming water is frequently above this temperature. In such cases, use of secondary disinfection should be considered.

Where sections of the system remain unused for long periods, for example an infrequently used shower in a hotel room, steps should be taken to run good quality water through these areas to waste for several minutes, at least weekly or for sufficient time to ensure the whole pipe length has been flushed. However, where sections of a system have not been used or flushed, then it is recommended that a disinfection procedure be performed before use. This process should reduce the risk of exposure to biofilm and possibly *Legionella* that might have colonized the water distribution system. Alternatively, if it is determined that sections of a system are to remain unused for extended periods, for example where staffing levels on-site have reduced the need for outlets, then consideration must be given to isolating these sections and possibly removing piping and fixtures completely.

In an effort to maintain cleanliness, tanks should be cleaned and disinfected if there is visual evidence of accumulation of deposits, sludge, or other contamination. The water surface should be free of deposition, and the tank lid should be in a good condition and fit tightly. An insect/vermin screen should be installed, and thermal insulation should be sound and in good condition.

Review of Control Measures for Hot and Cold Potable Water Systems

Potable hot and cold water systems should also implement a *Program*. This *Program* should detail the control scheme, identify tasks to be undertaken, frequency of the task, and the specific location (often by asset number) of the asset. This allows records to clearly identify what work was done and where.

Earlier in the chapter, the consequence of allowing water to remain still and possibly stagnate was discussed. Water turnover within the tank on a typical day should be monitored annually to ensure that operational changes have not affected water usage. For example, it is common practice for doctors and nursing staff to use alcohol gel to wash their hands between patients. Studies have identified that this practice, primarily introduced to restrict the spread of the methicillin-resistant *Staphylococcus aureus* (MRSA) bacteria, has resulted in less water usage contributing to water age or stagnation. Extra consideration now has to be given to any chance of *Legionella* proliferation within the distribution systems.

Although dependent upon design, internal inspection of water heaters should be undertaken annually, and cleaning and disinfection should be performed if there is evidence of scale or sludge accumulation. Frequently access is limited, and in such cases, water heater temperatures should be checked monthly. Temperatures obtained during thermal disinfection should be checked periodically and results recorded.

In order to ensure that no isolated contamination develops in localized areas of the distribution system, water temperatures of a representative number (e.g., 10–20% of the total number of outlets) should be checked annually on a rotational basis, and a representative number, normally those nearest to and furthest from the water heater, should be checked monthly (so-called sentinel or distal taps). Temperature checks should be taken after running for one minute at full flow for hot taps and two minutes at full flow for cold taps.

Hot water temperature should attain more than 50°C (122°F), while cold water temperature should attain less than 20°C (68°F) or <25°C (77°F), depending on local requirements. This ensures that the whole system is reaching satisfactory temperatures for *Legionella* control.

Thermostatic mixing valves may be used to prevent scalding and considerations should be given to the uses of these devices. Preferably, thermostatic mixing valves should be installed as close as practical to the point-of-use so that hot water can be delivered throughout the entire distribution system at or above 51°C (124°F). Where centralized thermostatic mixing valves are used to reduce water temperature, the blended water temperature should be high enough to maintain a minimum of 51°C (124°F) throughout the distribution system to the point-of-use. However, maximum allowable temperatures may be limited by codes intended to prevent scalding.

Microbiological Monitoring of Hot and Cold Potable Water Systems

Generally, those systems fed with potable water do not require significant microbiological testing. However, such testing forms a useful part of a control scheme, especially if taste or odor problems occur, high temperatures occur in cold water, or correspondingly low temperatures occur in hot water. Where biocides are used as the primary *Legionella* control process and temperatures are reduced, monthly to quarterly *Legionella* samples are recommended to ensure that the control regime is effective. This evidence must be recorded in appropriate site documentation.

In addition to the above recommendations, it would be considered good practice to undertake sampling for both *Legionella* and total heterotrophic aerobic bacteria in systems determined by the risk assessment as high risk. This includes areas such as hospital wards and retirement homes, for example. Testing frequency may be stipulated by local guidance for such premises.

Cleaning and Disinfection of Potable Water Distribution Systems

Cleaning and disinfection of potable water distribution systems are required under a number of circumstances. This procedure may be required in response to visual inspection of water tanks or heaters, temperatures within the system that do not meet recommended control parameters, physical alteration of the system, poor microbiological analysis results, or in an outbreak situation where the risk control program may have been compromised (see Figs. 21.7 and 21.8).

When chemical or thermal disinfection is conducted, warning notices must be posted. Physical barriers or tape may be necessary, depending upon site requirements. Chemical disinfection usually is performed using chlorine. In principle, procedures for cleaning and disinfecting new systems or refurbished systems are similar.

Following disinfection, tanks should always be filled with fresh water in order to remove water contaminated with debris.

Figure 21.7 Poorly controlled system with excessive micro and macro biological growth.

Figure 21.8 Contaminated section of system.

Records

In legal situations, records are often referred to as "evidence that speaks." Interpretation of this comment in relation to *Legionella* risk reduction is to infer that any records or communication between different parties should be filed and maintained to provide evidence that a particular issue was addressed. If no records are available, then some governmental regulation bodies might assume the work was never done. Hence, all appropriate records of monitoring and subsequent action should be kept and maintained for at least a five-year period to demonstrate compliance with regulations. Records should be maintained in order to demonstrate effectiveness of the risk management program, for all systems being considered within the risk

Records	Content
Risk assessment document and subsequent remedial actions	Consideration of factors such as proliferation potential, aerosol production potential, susceptible populations, and management procedures and corrective actions.
Name and position of people who performed assessment and their qualifications	Details to demonstrate competence.
Water management program for reducing risk	Identification of responsibilities and details on process management.
Details on personnel and lines of communication	Contact details of all management levels and flow diagram for management processes.
Records of plant use	Identification of normal plant operational factors for trend analysis.
Records of work carried out by site or contractors	What work undertaken and by whom.
Defect/action logs, Escalation program	Investigative records and process for deviation from key process indicators (KPI).
System description	Including diagrams and schematic drawings, identification of water supply tanks, inventory of fittings, identification of relevant items of pretreatment plant, and system volume.
Details of inspection procedures	Daily checks on equipment, chemical levels, etc.
Logbook	Records of water temperature, operation of pretreatment plant, inspection and test results, cleaning and disinfection operations, works undertaken on the system, works undertaken as a result of inspections or testing (defect/action log), all signed by the person performing the work.
Training records	To demonstrate competency by knowledge and skills.

TABLE 21.2 Typical Hygiene Records to Maintain

management plan. Table 21.2 lists typical records that would normally be maintained for a hygiene-based control program.

Other Risk Systems

Many water-containing utilities have been identified as a possible source of risk for legionellosis. Decorative fountains, machine coolant systems, and spas are but a few of the systems where potential risk has been identified. In each case, the same basic assessment principles can be applied:

- Does the system contain and support proliferation of *Legionella*?
- Is aerosol production likely?
- If so, who is likely to inhale the aerosol?

Incident analysis after an outbreak situation often identifies critical defects in the risk reduction program. Frequently, repeat nonconformances combine to exacerbate the situation.

Consequence of Outbreak

The worst-case scenario is where exposure has led to illness and possibly fatalities. In such situations, government authorities conduct a thorough investigation to identify any breach of health and safety guidance or where employees and public have been put at risk. In such an event, all records are reviewed in order to determine any lapse in the control plan. A site procedure containing a detailed process to deal with all eventualities is deemed good practice.

Training

Previous outbreaks of Legionnaires' disease have identified a lack of training and understanding of specific requirements needed to ensure that the risk management plan remains effective. Everyone involved in operation and maintenance of cooling water, potable water, and other risk systems should be aware of local guidance, and the need to be able to demonstrate that the individual has been trained to undertake their role in the control process effectively and competently. This includes the requirement for refresher training.

Conclusion

Reducing the risk from exposure to *Legionella* has warranted significant review, such that many countries have produced national guidance on how to introduce, monitor, and record preventative control programs. In addition, WHO has produced a general guidance document to cover many different types of facilities. For each utility, the same process of assessment of risk can be made (e.g., Does the system support the growth of *Legionella?* Does the system produce an aerosol?; Will susceptible people be exposed to it?). By understanding the different interrelating factors that combine to create a risk, and specifically by proactive management, legionellosis can be a preventable disease and exposure to risk reduced.

SECTION 3.5

Applications—Post-Treatment

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CHAPTER 22

Primary Effluent Treatment

Industrial effluent treatment systems take many forms, depending on the constituents in the effluent and the goals of the treatment (discharge requirements). Primary treatment, as the name implies, precedes any additional treatment such as biological processes (secondary treatment). The primary treatment may be the only treatment, when the final discharge is to a publicly owned treatment works (POTW), or the treated water meets recycle requirements, such as blast furnace scrubber water in the steel industry. Primary treatment may be preceded by bar screens, grit (sand) removal, equalization basin, and pH correction to protect subsequent equipment and processes.

Effluents contain many different types of organic and inorganic solids, both dissolved and suspended depending on the effluent sources. Physical–chemical processes are used to remove specific dissolved matter in the effluent, such as heavy metals and emulsified oils, and to oxidize or precipitate toxic chemicals. These processes may include sedimentation or dissolved air flotation (DAF).

Clarification by Sedimentation

Clarification of effluent through the process of sedimentation is the separation of suspended solids by gravitational settling. The sedimentation process is used in primary settling basins, removal of chemically treated solids, and solids concentration. Sedimentation basins perform the twofold function of producing both a clarified water product, and a concentrated slurry (sludge) product. Two distinct forms of sedimentation vessels are in common use. The clarifier is used, as the name suggests, for the clarification of a dilute suspension to obtain water containing minimal suspended solids, while producing a concentrated sludge. A thickener is used to thicken a suspension to produce an underflow with a high solids concentration, while also producing a clarified overflow. Primary clarification is the most economical unit process for pollutant removal from a cost per unit weight of biochemical oxygen demand (BOD) or solids removed. For this reason, it is the most widely used process for effluent treatment.

Forms of Solids in Effluent

Total suspended solids (TSS) in water are defined by the U.S. Environmental Protection Agency (EPA) as those dry solids retained on a 0.45 µm filter from a total water sample and reported as dry mg/L or percent dry solids by weight. (The suspended solids include floatable material.) The soluble or dissolved solids in the water are those that pass through the 0.45 µm filter and reported as dry mg/L or percent dry solids by weight. The sum of these two is the total solids in the water. By burning the solids of each, the suspended solids and dissolved solids are further classified into volatile and nonvolatile. The volatile fraction is assumed to represent the organic fraction in the suspended and dissolved solids.

The TSS in the water are additionally divided into settleable solids and nonsettleable solids. The nonsettleable solids are the fine, colloidal particle fraction held in suspension by surface charges that do not settle by gravity. Clarification processes remove only the settleable fraction of the suspended solids. If nonsettleable solids are to be removed by clarification, chemical conditioning (coagulation and flocculation) of the colloidal solids is necessary.

Standard Methods for the Examination of Water and Wastewater (American Public Health Association, Washington, DC) includes two methods for the measurement of settleable solids. The first is reported by volume as mL/L and the second is by weight in mg/L.

A one-liter Imhoff cone is used to settle a mixed sample of the effluent for one hour. The volume of solids that settles in the cone is read by the milliliter graduations on the cone apex. The settleable suspended solids are reported by volume as mL/L.

The nonsettleable solids by weight are measured by settling a minimum one-liter sample in a minimum 90 mm diameter glass vessel. A larger diameter vessel and sample may be used, but the sample depth in the container must be deeper than 200 mm. The sample is allowed to settle for one hour. A 250 mL sample is siphoned from the center of the container at a point halfway between the surface of the settled solids and the water surface without disturbing the settled or floating material. The suspended solids by weight (mg/L) are determined on the 250 mL sample, and this represents the nonsettleable solids. The settleable solids by weight are then the difference between the mg/L TSS and the mg/L nonsettleable suspended solids.

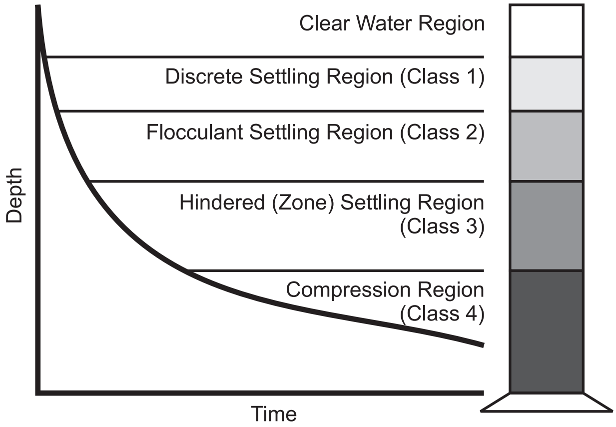


Figure 22.1 The four types of settling.

Sedimentation Phenomena

Four basic classes or types of sedimentation processes take place, depending on the particle concentration and the degree of particle interaction. These settling classes are discrete particle, flocculant, hindered (also called zone), and compression (Fig. 22.1). More than one class of settling can take place at any one time, and it is common to have three occurrences in the clarification of dilute solutions. Thickening of solutions having suspended solids concentrations greater than about 500 to 1000 mg/L typically utilizes hindered and compression settling. Table 22.1 describes these types of settling phenomena.

Type of Settling	Description	Application
Discrete particle (Class 1)	Particles in a low solids concentration settle as individual entities not interacting with adjacent particles.	Removal of grit, sand, and inorganic particles such as slag in steel mills.
Flocculant (Class 2)	A dilute suspension of particles that coalesce or flocculate during sedimentation. The particles increase in size and mass by agglomeration, thereby increasing the settling rate.	Most solids in effluent are of a flocculant nature including pulp and paper, food processing, municipal, and biological treatment. Chemically treated solids exhibit Class 2 sedimentation.

Table 22.1 Types of Sedimentation in Effluent Treatment

Type of Settling	Description	Application
Hindered or Zone (Class 3)	Suspensions of intermediate concentration in which the forces between particles are sufficient to hinder the settling of adjacent particles. The particles adhere together, and the mass settles as a blanket, forming a distinct interface between the floc and the supernatant. The settling rate starts to decrease.	Hindered settling is characterized by biological solids and flocculated chemical suspensions, when the concentration exceeds 500–1000 mg/L, depending on the type of particle.
Compression (Class 4)	The particle suspension has reached a concentration such that a structure is formed and further settling can occur only by compression of the structure. The weight of the particles being constantly added to the top of the structure by sedimentation provides this compression. The settling rate of this zone becomes very slow.	Occurs in the lower layers of deep sludge masses, such as in the bottom of deep clarifiers and in sludge-thickening facilities.

Table 22.1 Types of Sedimentation in Effluent Treatment (*Continued*)

Discrete Particle Settling

The analysis of discrete, nonflocculating particle settling is by means of the classic laws of sedimentation formed by Newton and Stokes. Newton's Law relates the gravitational force on the particle, with the frictional resistance or drag, and the difference between the densities of the particle and liquid. The value of the drag coefficient varies depending on turbulent or laminar flow conditions and is a function of the Reynolds number. The drag coefficient becomes a constant for the low laminar flow conditions found in clarification. Stokes incorporated this constant drag coefficient into Newton's gravitational force equation to arrive at the classic Stokes' Law for sedimentation:

$$V_o = \frac{G(\rho_1 - \rho_2)D^2}{18\mu} \qquad (22.1)$$

where V_o = settling velocity, cm/s
G = gravitational force, cm/s^2
ρ_1 = particle density, g/cm^3
ρ_2 = liquid density, g/cm^3
D = particle diameter, cm
μ = liquid viscosity, dyne · s/cm^2

A terminal velocity V_o is selected for the sizing of a sedimentation basin so that all particles having a velocity equal to or greater than V_o are removed. Class 1 settling in an ideal basin is shown in Fig. 22.2. The particle having a settling velocity V_o that settles through a distance equal to depth D in length L (theoretical detention period) is removed. This is called the basin overflow rate:

$$V_o = \frac{Q}{A} \tag{22.2}$$

where Q = inlet flow rate, gpm or gpd (m^3/h)
A = surface area of tank, ft^2 (m^2)
V_o = overflow rate, gpm/ft^2 or gpd/ft^2 (m^3/[h · m^2] or m/h)

In the ideal basin of Fig. 22.2, it is assumed that particles entering the tank are evenly distributed over the inlet cross-section, and a particle is considered removed when it enters the sludge zone. Thus, all particles with a settling velocity greater than V_o are removed, and particles with lower settling velocity (V_p) are removed in the ratio V_p/V_o as illustrated in Fig. 22.2.

The flow capacity of basins for discrete particle settling is independent of depth, as shown in Eq. (22.2). The length of the basin and the time that a unit of water is in the basin for continuous flow sedimentation needs to be such that all particles with the design velocity of V_o settle to the bottom. The design velocity V_o for a full-scale continuous flow clarification device must be adjusted for the effects of influent and effluent turbulence, hydraulic short-circuiting, sludge storage, velocity gradients due to temperature changes, and operation of sludge removal equipment.

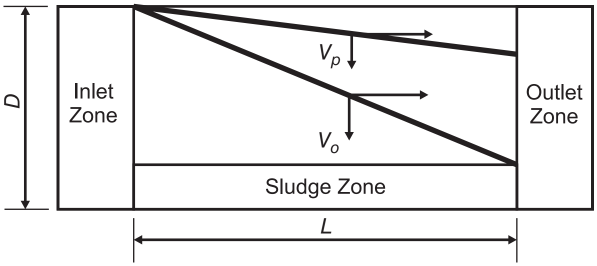


FIGURE 22.2 Discrete particle settling.

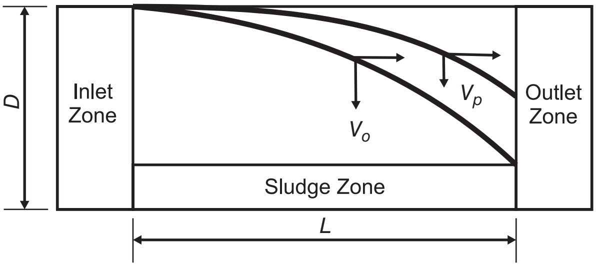


FIGURE 22.3 Flocculant settling.

Flocculant Settling

Flocculant settling is created by the coalescence of particles in a dilute solution. The settling velocity of the particle increases as it settles through the tank depth, because of this agglomeration that increases its size and density. Figure 22.3 illustrates the curvilinear settling path of the particle as it increases in settling velocity and size. Most of the suspended solids in industrial effluents are flocculant in nature. The efficiency of removal for discrete particles is related only to the overflow rate, while flocculant particle removal is dependent on both overflow rate and depth of basin (detention time).

The degree of flocculation that takes place is dependent on the opportunity for particle contact, the overflow rate, the depth of basin, initial particle concentration, range of particle sizes, and flocculating nature of the particles. A mathematical analysis concerning these parameters for basin design and operation is generally considered impossible. Long column settling tests are required to determine the effects of these variables, when historical data concerning the type of solids in a specific type of effluent is unknown. The columns used are typically 6 inches (152 mm) in diameter by 8 to 10 ft (2.4–3 m) high.

Hindered Settling

Hindered settling is typified by activated (biological) sludges and chemically flocculated suspensions, when the concentration of solids exceeds 500 to 1000 mg/L. Hindered settling takes place following the concentration of the suspension during flocculant settling or in gravity thickening, when the initial solids concentration is greater than about 500 mg/L. Since flocculated particles are in close proximity to each other, they settle as a mass or blanket, and form a distinct water/solids interface at the top of the blanket. The friction produced as the water moves up through the interstices of the blanket slows the settling rate of the mass (Fig. 22.4). The reduction in settling rate continues as the solids blanket concentrates. The rate of settling in the hindered region is a function of the concentration of solids and their characteristics.

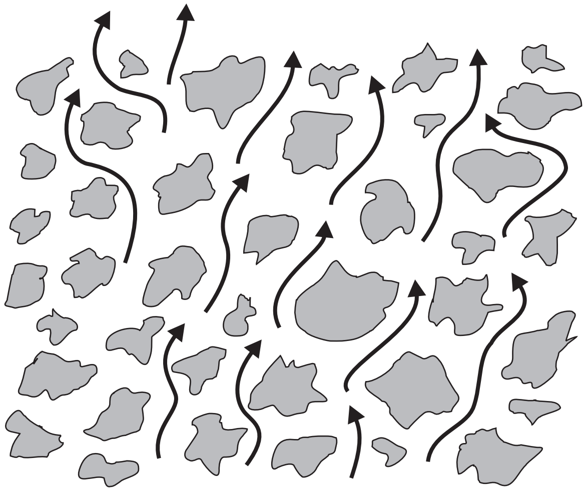


Figure 22.4 Hindered settling.

Compression Settling

A compressed layer of solids starts to form beneath the hindered settling zone as sedimentation continues. A structure is formed in this region by the close physical contact between the particles. Additional water is forced out and upward from the hindered settling zone, by the increasing weight of solids on the top of the zone as sedimentation continues. The maximum solids concentration of the solids at the bottom is limited by the characteristics of the solids and the weight of solids above the lowest layer.

Due to the many variables between the various types of solids encountered in effluent treatment, settling tests are usually required to determine the settling rate and detention time when hindered and compression settling are a consideration. The test cylinder is equipped with a slow-speed stirrer rotating at 4 to 5 revolutions per hour. The stirrer simulates the rake action and corresponding hydraulic motion in a clarifier. This breaks the arching action of the solids in these zones, to increase the release of water from the sludge bed, and increase solids concentration (Fig. 22.5).

Mass Loading

Both the clarification of the water overflow and the thickening of the sludge underflow are involved in the separation of flocculant suspensions. The overflow rate for clarification requires that the rise in velocity of the liquid overflowing the tank be less than the settling rate of the suspension. The tank surface area requirements for thickening of the underflow to a desired concentration are related to the

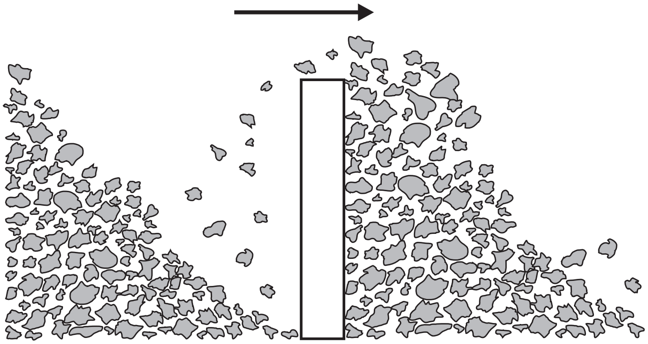


FIGURE 22.5 Rake action in compression zone.

solids loading or solids flux, usually expressed in terms of mass loading (pounds per square foot per day or kilograms per square meter per day) or a unit area (square feet per pound of solids per day or square meters per kilogram of solids per day). The mass loading with corresponding underflow concentration for a particular application can be calculated from a stirred laboratory test.

In most clarification applications, the limiting flux and underflow concentration from the laboratory, testing must be equal or be greater than the solids loading rate to the clarifier:

$$G_L = \frac{C_o Q_o}{A} = \frac{M}{A} \tag{22.3}$$

where Q_o = influent flow, $\mathrm{ft^3/d}$ ($\mathrm{m^3/d}$)
C_o = influent solids, $\mathrm{lb/ft^3}$ ($\mathrm{kg/m^3}$)
M = solids loading, lb/d (kg/d)
G_L = limiting solids flux, $\mathrm{lb/[d \cdot ft^2]}$ ($\mathrm{kg/[d \cdot m^2]}$)
A = area, $\mathrm{ft^2}$ ($\mathrm{m^2}$)

Both gravity and the velocity resulting from sludge removal at the tank bottom in a continuous clarifier or thickener remove solids:

$$U = \frac{G_L}{C_u} \tag{22.4}$$

where U = downward sludge velocity due to sludge removal, ft/d (m/d)
C_u = underflow concentration, $\mathrm{lb/ft^3}$ ($\mathrm{kg/m^3}$)

Increasing the underflow pumping rate U in Eq. (22.4) decreases the underflow concentration C_u. The solids flux G_L is not the limiting factor for most clarification applications, since the influent suspended solids are generally less than 500 mg/L.

Clarifier Hydraulic Capacity

The parameters that affect the settling rate are of prime consideration for the sizing and operation of a sedimentation device. The larger the particle diameter, and the heavier the particle, the faster it settles. The colder the water (higher viscosity), the slower the settling rate. Effluents contain a mixture of particle sizes and densities. Therefore, the sedimentation device should be sized for the smallest, lightest settleable particle, in order to maximize the settleable solids capture. Conversely, a change in an industrial process to one that produces a larger quantity of smaller lighter particles results in a decrease in solids capture.

A sedimentation device that includes inlet baffling for the dissipation of the influent energy, a quiescent zone for particulate settling, mechanical means for the removal of settled solids, and low flow velocity to the outlet, is commonly called a clarifier. The hydraulic capacity of a clarifier is based on the discreet and flocculant type settling velocity expressed as feet per minute (meter/hour). In US units, multiplying the settling rate by 7.48 gal/ft^3 yields the hydraulic loading expressed as gallons per minute per square foot. The hydraulic loading can also be expressed as gallons per day per square foot. The metric units are cubic meters per hour or day per square meter. This hydraulic loading is also called the overflow rate, and it is used to size a new clarifier or ascertain the capacity of an existing clarifier.

A settling curve is developed for a sample of the effluent to arrive at an estimate of the overflow rate. Preferably, a minimum two-liter graduate is used for the settling test, and the fall of the suspended solids in milliliters is recorded for each 30 seconds of elapsed time. Readings are taken for at least 30 minutes or until the change in solids height per minute is relatively small or constant. The results in milliliters are converted to inches (millimeters) by measuring the graduate (inches/2000 mL or mm/2000 mL) and graphed as illustrated in Fig. 22.6. The slope of the linear portion of the curve is the settling rate for that sample in inches per minute (mm/min).

In the Fig. 22.6 example, the slope is (2–16)/(9–0) = –1.56 inches/min (–39.51 mm/min) yielding a negative slope as it should be when we are measuring the fall of suspended solids. In our hydraulic loading calculation below, we will be using the absolute value of the slope for the calculation. It is necessary to apply a scale-up factor to account for the dynamics of an operating clarifier versus the quiescent state of the settling test. The scale-up factor is generally in the range of 0.65 to 0.85, depending on the actual application conditions. The hydraulic loading can then be calculated as follows:

US Units (1.56 in./min)(1 ft/12 in.)(7.48 gal/ft^3)(0.7) = 0.68 gpm/ft^2 or 980 gpd/ft^2

Metric Units (39.51 mm/min)(1 m/1000 mm)(60 min/h)(0.7) = 1.66 m^3/[h $\cdot$ m^2] or 39.8 m^3/[d $\cdot$ m^2]

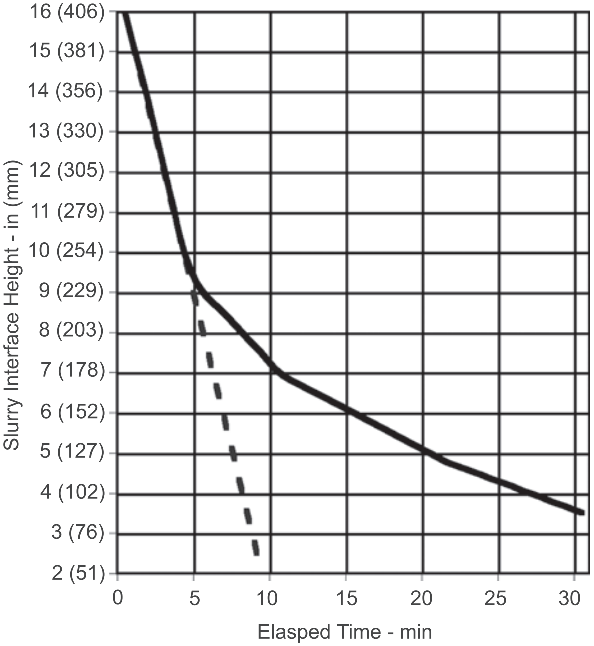


Figure 22.6 Settling curve.

The sedimentation device can be referred to as a clarifier-thickener, when thickening of the settled sludge is desired. Determining the settling rate of the sludge bed to achieve the target sludge concentration is important to learn if this rate controls the capacity of the clarifier-thickener. The dry solids loading or solids flux, expressed as pounds dry solids per square foot per hour or day (kilograms dry solids per square meter per hour or day), is the parameter used to describe the thickening capacity. (A typical example is a secondary clarifier following a biological aeration basin, where the solids loading and not the hydraulic loading is the controlling factor.) The concentration of the settling sludge bed takes place during and after the knee in the settling curve (Fig. 22.6), where hindered and compression zone settling take place. Generally, the solids flux is not a controlling factor in clarification of effluents having dilute solids concentrations less than about 500 to 1000 mg/L.

Another major parameter for sizing a clarifier is the minimum tank depth or detention time. The tank volume must provide the required flocculant settling depth plus 3 to 4 ft (0.91–1.2 m) for deceleration of the water as it approaches the effluent weirs, plus depth for sludge storage. The water depth at the tank wall is commonly 8 to 15 ft (2.4–4.6 m), with a minimum basin floor slope of 1 on 12.

Degrees F	Degrees C	Correction Factor
32	0	0.63
40	4.4	0.73
50	10.0	0.86
60	15.6	1.00
70	21.1	1.15
80	26.7	1.31
90	32.2	1.48

Table 22.2 Temperature Correction for Rise Rate

The typical detention time is in the range of 1.5 to 3 hours. Slow-settling solids usually require a deeper water depth with correspondingly longer detention times.

Temperature

Warm water has a lower viscosity (less dense) than colder water. Therefore, the particle settling rate is faster at higher water temperatures than colder ones. Raising the temperature from 32 to 80°F (0–27°C) doubles the settling rate for a given particle, since both the density and viscosity of the water are reduced. Multiply the rise rate by the correction factor in Table 22.2 to adjust for the change of water temperature from 60°F (15.6°C).

Another temperature concern is the possibility of developing thermal gradients within the clarifier. If developed, they can prevent the sedimentation of the suspended solids or lift settled solids, from the sludge blanket up to the outlet launders. This is of concern when treating warm waters in above grade steel tanks, in cold climates. The water at the tank wall and floor cools, so that the bottom of the tank has a colder water temperature then the incoming water. The warmer influent water can short-circuit to the effluent launders, resulting in high solids carryover. In warmer climates, above ground clarifiers can absorb radiant heat from the sun, and clarifier water temperatures increase. When cooler influent water enters the clarifier, the temperature difference can create thermal currents, which can result in resuspension and carryover of settled floc.

Clarifier Operating Principles

The operating zones in a clarifier are a zone of clear water, the sedimentation zone (discrete and flocculant settling), and the thickening zone as illustrated in Fig. 22.7. The depth of the thickening zone

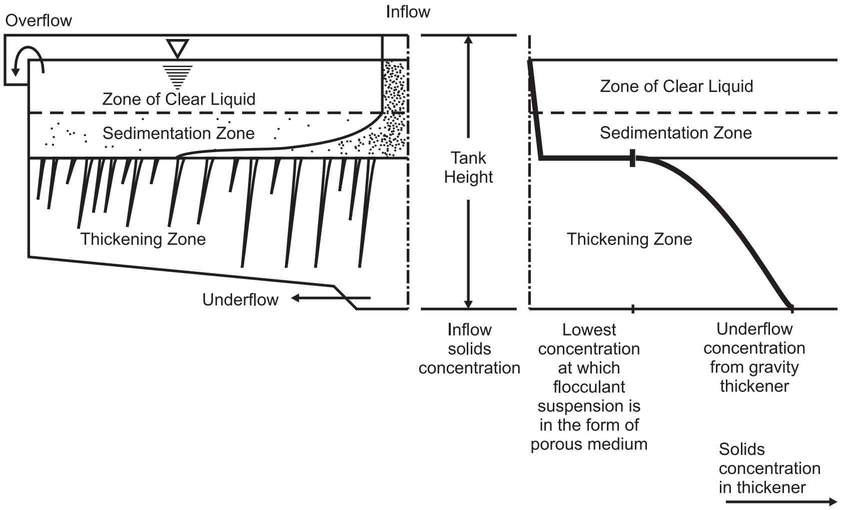


Figure 22.7 Clarifier operating zones.

(sludge bed) is dependent on the depth of the tank allocated for sludge thickening. The water inlet must always be above the sludge bed (thickening zone) for high efficiency solids capture. Solids can be carried to the outlet launder, if the feed goes through the top of the sludge bed. The objective is to operate the clarifier with as low a sludge bed depth as possible, yet still produce a high underflow sludge solids concentration, if needed.

The solids mass balance around the clarifier must be maintained at all times. The influent settleable dry solids less, the effluent settleable dry solids, plus the underflow dry solids, must be zero, to keep the continuous operation of the clarifier in balance. The required underflow sludge pumping volume can be estimated by the influent settleable solids, less the effluent settleable solids in mL/L times the influent flow.

The solids inventory (sludge bed) in the clarifier becomes greater with an increase in the influent solids, or a decrease in underflow pumping. If not corrected, this imbalance results in an increase in the effluent solids. For example, plants that store sludge in the clarifier to meet an eight-hour per day sludge dewatering schedule classically have increased effluent solids when not dewatering. Likewise, trying to store sludge in the clarifier over a weekend can be disastrous, particularly if the settled solids contain organic material. The organic material can undergo anaerobic decomposition producing methane and hydrogen sulfide gases, which can float the settled solids. Organic solids should not be kept in the clarifier longer than 24 hours.

Sludge Bed Depth Measurement

Regular measurement of the sludge bed depth is an easy way to maintain the clarifier solids balance. An increase in sludge bed depth indicates that the underflow blowdown needs to be increased, while a decreasing depth shows that the underflow pumping can be decreased. The best operation is one that can pump the underflow continuously to subsequent sludge handling facilities, instead of an on/off pumping schedule.

The sludge bed depth can be measured manually using a sludge judge. This is a clear plastic tube having feet or meter graduations with a check valve at the bottom. A core sample of the sludge bed is taken with the sludge judge and the depth of the sludge read on the side of the tube. This measurement always should be taken at the same place on the clarifier walkway or wall, since the floors of clarifiers are generally on a slope.

Automatic sludge bed indicators are also available. Some are a probe type based on the transmission and receiving of an infrared beam, while others are based on sonics. The sonic transmitter and receiver are located at the water surface, and the face of the instrument's control panel indicates the profile of the clarifier depth and sludge bed, much like a fish finder. The infrared types of indicators do not work in situations where the water is highly colored. Either type of indicator can be used to automatically control the underflow pumping, to continuously keep the sludge bed depth and thus the solids balance, in the optimum range.

The rake drive torque can be used as a surrogate for the sludge bed depth in large clarifiers handling settleable solids with a high specific gravity, such as in the steel and paper industry. The rake drive torque usually goes up as the sludge bed depth increases. The motor amps cannot be used for the bed depth indication, since the rake drive unit is geared down to such a low speed.

Influent Flow Control

Continuous measurement and recording of the influent flow to a clarifier indicate the instantaneous hydraulic loading and changes with time. Flow rates greater than the design overflow rate result in an increase in the effluent solids. Rapid, short-term, large increases in the flow rate need to be avoided, since the resulting hydraulic surge can wash solids out of the clarifier. It may take a clarifier as long as two hours to recover from such a surge.

Effluent discharged to the primary clarifier is often quite variable, due to storm water and intermittent discharges from an industrial plant. An equalization basin is often provided to even out these variations in both flow and composition. The most efficient solids removal occurs when constant flow is treated within the clarifier's design rating.

On/off level switches may control the forwarding pumps from the equalization basin or the pump station wet well, which is poor practice.

The influent pumps need to be controlled to eliminate the clarifier surging created by this on/off control. One method is to use a modulating valve that is controlled by the basin or wet well level that regulates the pump discharge directly to the clarifier, or recycles a portion of the flow back to the basin or wet well in order to keep the clarifier influent close to a constant rate. Another method for multiple pumps is to have a baseline constant speed pump or pumps in conjunction with a variable speed pump or a third pump, which has a modulating discharge throttling valve. The pump speed or discharge throttling valve is adjusted proportionally to the level in the wet well or equalization basin, so that the clarifier influent flow rate is gradually adjusted to eliminate high peak flows while maintaining the hydraulic loading within the design value.

Hydraulic devices such as overflow weirs and gates must divide the flow equally to multiple clarifiers. One clarifier in the group can become hydraulically overloaded with a poor division of the total flow. Dye or diagnostic TRASAR® chemistry tests can be used to check and adjust flow distribution.

Chemical Treatment

Chemical treatment of the clarifier influent can be used to increase removal of suspended solids, by flocculating the colloidal nonsettleable solids to convert them to settleable ones. Depending on the degree of overloading, problems associated with high hydraulic or solids loading can be alleviated by chemical treatment.

Coagulants and/or flocculants may be used, depending on the industry and the goals of the chemical treatment. The coagulants may be inorganic salts, such as iron or aluminum, organic polymers having various formulations, or a blend of organic and inorganic. Anionic, nonionic, or cationic polymer flocculants are used alone or following a coagulant. The polymer flocculants are available in different molecular weights for each charge family. Polymer flocculants, besides increasing the clarity of the effluent, may also increase the underflow sludge concentration, depending on the chemical dosage.

The appropriate chemical program for a specific installation is ascertained by jar testing. The coagulant, if used, is generally added upstream from the clarifier at a point with high energy mixing, such as the suction side of the clarifier feed pump. The long molecular chain flocculants cannot withstand high energy mixing, since the molecular chain can be sheared. The flocculant is typically added just outside the clarifier or into the clarifier feed well.

Types of Sedimentation Clarifiers

Circular, rectangular, plate (also called lamella), drag, and oil/water separators are the basic types of sedimentation clarifiers. The parameters previously discussed in general for sedimentation pertain to these units.

Circular Clarifiers

Circular center-feed clarifiers are the most common sedimentation configuration. Figure 22.8 illustrates the side inlet, bridge supported clarifier mechanism used for basins smaller then approximately 50 ft (15 m) in diameter. For basins 50 to 200 ft (15–61 m) in diameter, the clarifier mechanism is supported by a centrally located column, with the inlet pipe being beneath the floor and rising up through the

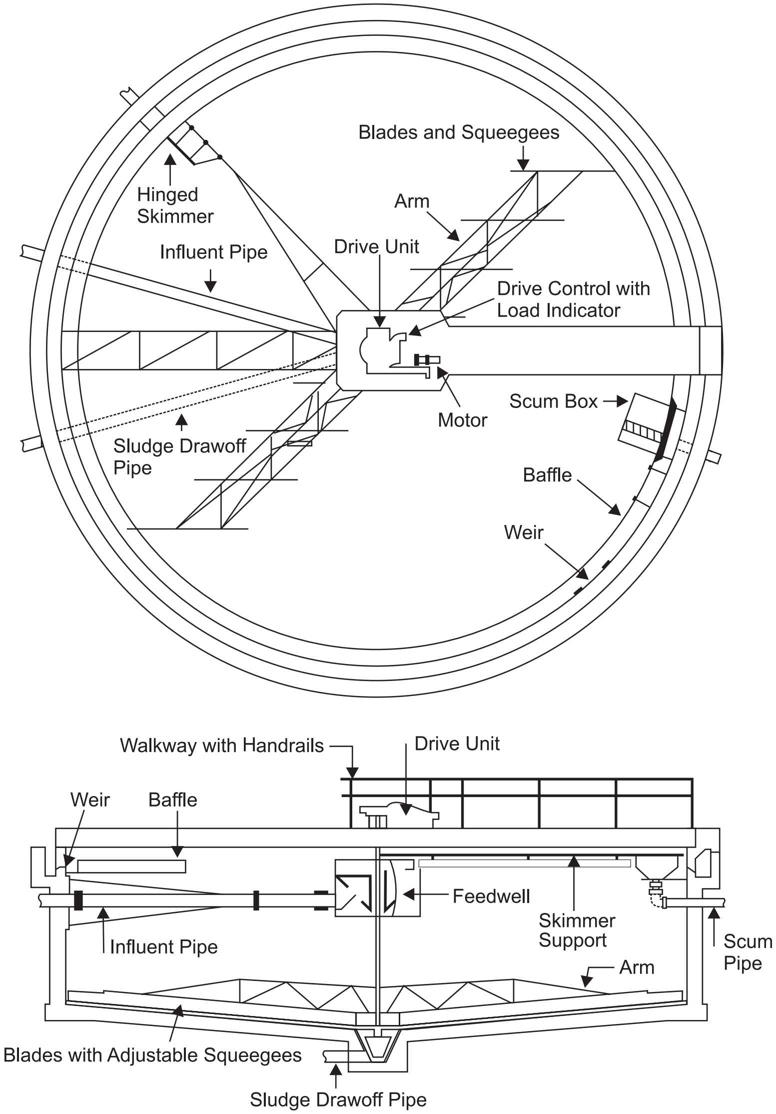


Figure 22.8 Center-feed clarifier. (*Courtesy of Envirotech.*)

column to the feed well. The center-feed clarifier has four distinct sections, each with its own function.

The inlet section or feed well of the center-feed clarifier provides a smooth transition from the high influent velocity to the low uniform velocity required in the settling zone. The feed well must be carefully designed to provide the necessary water velocity reduction to prevent turbulence and short-circuiting in the settling zone, with resulting solids carryover. The quiescent settling zone must be large enough to meet the overflow rate and depth requirements for discrete and flocculant settling.

The outlet zone provides a transition from the low velocity of the settling zone to the relatively higher outlet velocity, which is typically limited to values less than 14 gpm per linear foot (10.4 m^3/h per linear meter) of outlet weir plate. Treated water is typically discharged over v-notched weir plates, which serve two purposes. The v-notched weirs provide equal removal of the water from 360° of the periphery of the circular clarifier. The v-notches also maintain the water surface elevation in the clarifier close to constant for varying flow rates, which allows floating material to be skimmed from the surface.

The fourth section, the sludge zone, must effectively collect and compact the solids removed in the settling zone and remove this sludge from the clarifier without disturbing the sedimentation zone above. The floor is normally sloped at 1 on 12 to the center of the unit, where sludge is collected in a hopper for removal (blowdown). Mechanically driven sludge rakes or plows move the sludge down the slopping floor to the sludge hopper. The rakes are commonly driven from a drive unit located at the center of the tank. Another less frequent configuration uses a traction drive mounted on the top of the basin wall, which drives a rotating walkway that rotates the rakes and skimmer.

The peripheral-feed (rim-feed) clarifier (Fig. 22.9) attempts to use the entire volume of the circular clarifier basin for sedimentation. The influent trough width decreases from the influent location to a point 180° away, and has orifices in the floor spaced to distribute the flow equally around the tank periphery. Water enters the lower section at the periphery at extremely low velocity, providing immediate sedimentation of large particles. The velocity accelerates toward the center, and then decreases as the flow is reversed and redirected to the overflow weirs on the effluent trough, located inboard of the influent launder. This type of clarifier is sensitive to temperature changes and hydraulic load fluctuations, since the flow pattern depends entirely on inlet hydraulics.

Rectangular Clarifiers

The rectangular basin is somewhat like a section taken through a center-feed clarifier, with the inlet at one end and the outlet at the other. A typical rectangular basin has a length to width ratio of

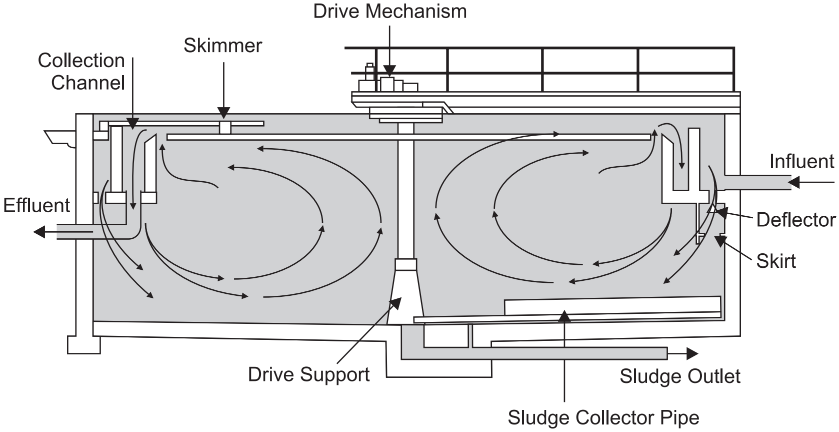


Figure 22.9 Peripheral-feed clarifier. (*Courtesy of Envirex, a Rexnord Company.*)

approximately 4:1. Flow through rectangular clarifiers enters at one end, passes through an inlet baffle arrangement, and traverses the length of the tank to the effluent weirs and troughs. Sludge removal is normally accomplished by a dual-purpose flight system (Fig. 22.10). The rake mechanism consists of two, parallel endless conveyor chains running the length of the basin, with rake flights (cross pieces) extending across the width of the tank attached between the chains. The settled solids are moved by the flights to the sludge hopper, typically located at the influent end of the basin. The flights on their return travel to the effluent end, serve as skimmers to remove floating material. The flight system moves very slowly to avoid turbulence, which could interfere with the settling process. The rotating scum trough removes floating material. The trough may be either manually operated or automatically rotated to remove the floatable material

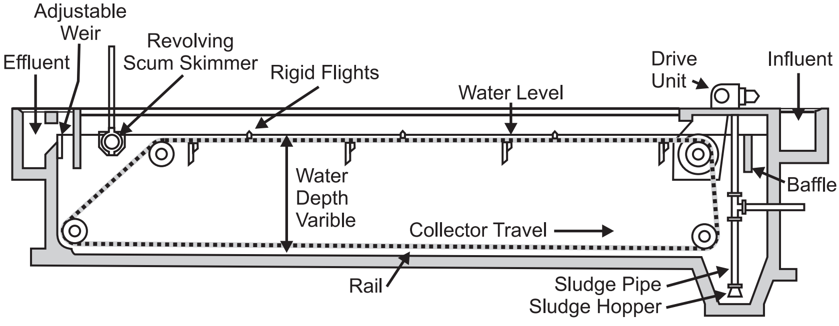


Figure 22.10 Rectangular clarifier.

Figure 22.11 Rectangular clarifiers with common wall construction and traveling bridge collectors. (*Courtesy of Walker Process Division, Chicago Bridge & Iron Company*.)

that accumulates at the lip of the skimmer. The chain and flight mechanism design limits the width of this type of rectangular clarifier to about 20 ft (6.1 m). Common walls can be used between multiple units to reduce construction costs (Fig. 22.11).

A single sludge scraper supported by a traveling bridge is used to move the sludge in wide rectangular basins. The bridge moves on rails mounted on the tank walls (Fig. 22.12). The bridge may be towed by cables or powered by a traction drive mounted on the wall. A skimmer is also supported from the bridge to move floating material

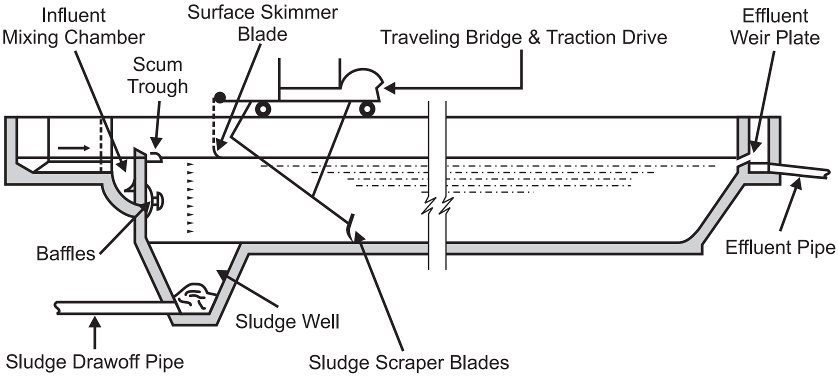


Figure 22.12 Traveling bridge mechanism.

to the scum trough that may be located at either the influent or the effluent end. The bridge and skimmer move material only in one direction and are retracted for the return trip to the opposite end.

The traveling bridge is generally provided with a programmable controller for the traveling cycles of the bridge. For example, the bridge may scrape the sludge in the first third of the basin two or three times (where a large quantity of solids settle), and then scrape the total basin length, then returning to the opposite side, and resting for a period before starting the cycle again. The best traveling cycle time is dependent on the type of effluent and the solids characteristics.

Settled solids may be collected in a single hopper, multiple hoppers, or in a transverse trench which has a hopper at one end for either the chain and flight, or traveling bridge sludge removal mechanism. The transverse trench may be equipped with a chain and flight collector or a screw conveyor to move the sludge to the hopper.

Circular sludge rake mechanisms are designed with pantograph extensions, so that the mechanism can rake the corners of a square basin. Two of these mechanisms are then used to remove sludge in rectangular basins (Fig. 22.13).

Parallel Plate and Tube Clarifiers

Prefabricated clarifiers that incorporate parallel plates or tubes on a slope are commonly used for smaller plant flow rates [less than about 1000 gpm (227 m^3/h)]. Figure 22.14 illustrates the Parkson Lamella® clarifier that incorporates a flash mix tank and a flocculation tank. The flow is introduced by means of a feed duct from the flocculation

Figure 22.13 Circular sludge collector with rakes designed for corner cleaning. (*Courtesy of FMC Corporation*.)

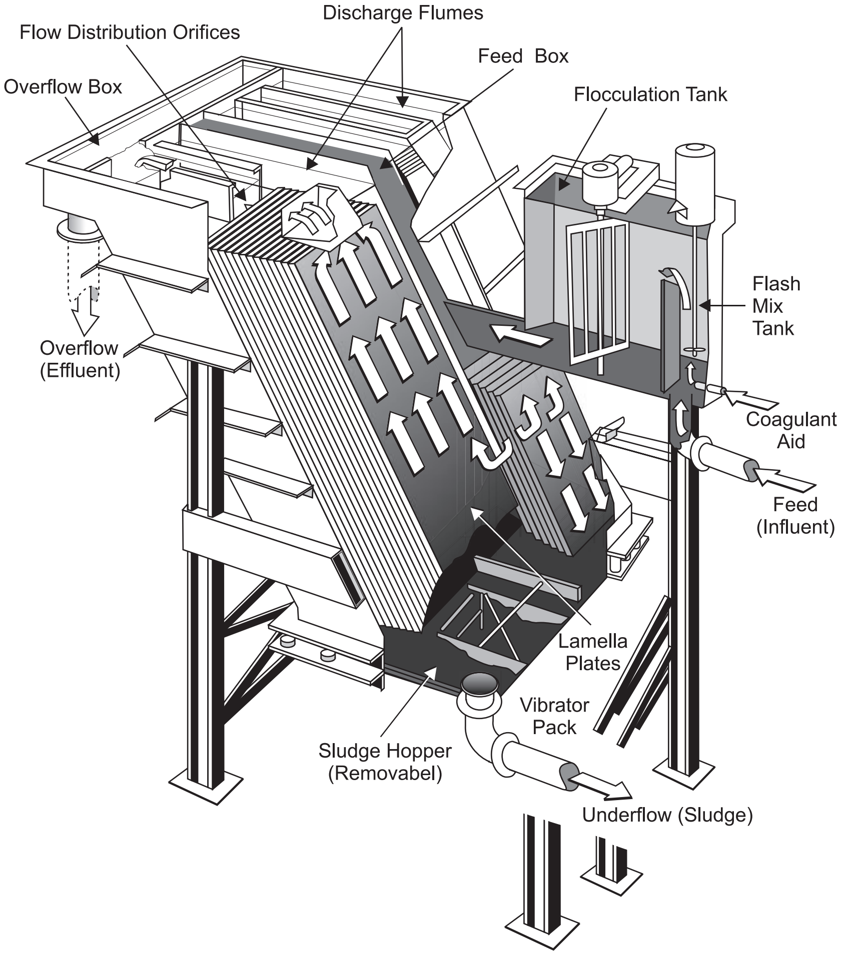


FIGURE 22.14 Parkson Lamella® clarifier. (*Courtesy of Parkson Corporation*.)

tank to the clarifier feed box, which is a bottomless channel between the plate sections. The flow is then directed downward to the individual side entry plate slots. The feed is distributed across the width of the plates and then flows upward under laminar flow conditions. The solids settle on the plate surfaces, while the clarified water exits from the top of the plates through orifice holes. These holes are placed immediately above each plate and are sized to induce a calculated pressure drop to ensure that the influent flow is evenly distributed among the plates. The solids slide down the plate surfaces into the sludge hopper, from where the sludge is removed. Flocculation is induced as the solids roll down the inclined surface.

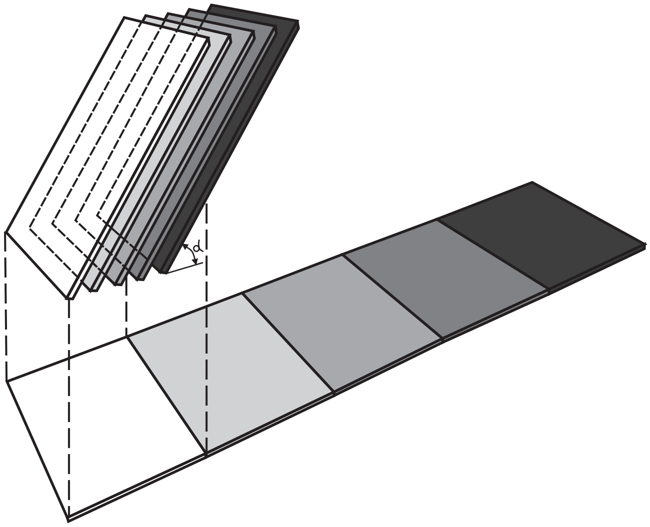


FIGURE 22.15 Plate clarifier floor area compared to a conventional rectangular clarifier.

The plates are spaced 2 to 4 inches (51–102 mm) apart and inclined 45 to 60° from horizontal, depending on the application and manufacturer. The total effective settling area is based on the horizontal projected area of each plate (Fig. 22.15). The total projected area is used to calculate the rise rate. The design rise rate for plate clarifiers is the same as for conventional clarifiers. The only advantage that a plate clarifier has over a conventional clarifier is that a large horizontal settling area can be provided in a small area of land or footprint. Figure 22.15 illustrates the area used for a plate clarifier as compared to the same area provided by a conventional rectangular clarifier. Some manufacturers use sloped parallel tubes instead of parallel plates, in which case the tube modules are referred to as tube settlers. The sedimentation principles for tube settlers are the same as for the parallel plate configuration.

Parallel plate sedimentation is based on both discrete and flocculant particle settling, and the overflow rate for the total plate projection area is determined by settling tests, the same as for conventional type clarifiers (Fig. 22.16). The parallel plate arrangement does not provide the necessary area and depth for hindered or compression settling. Its application is therefore limited to dilute suspensions having a maximum suspended solids concentration of approximately 500 to 1000 mg/L, depending on the application. The plate surfaces may have to be periodically cleaned, if the solids have a sticky nature and adhere to the plates. The accumulation of solids on the plate surfaces results in solids carryover, due to increased water velocity.

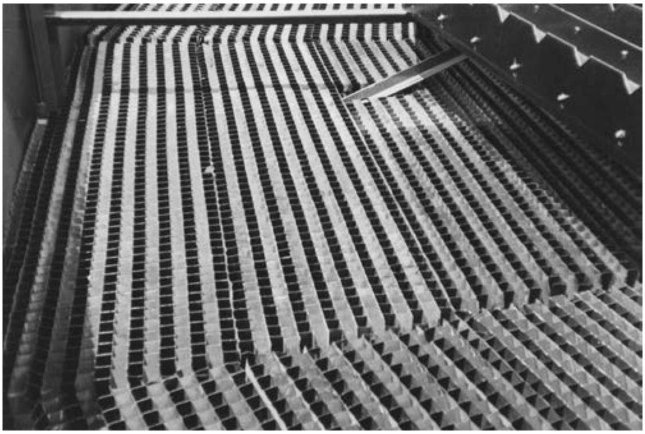


Figure 22.16 Plastic tube modules installed in an existing conventional clarifier. (*Courtesy of Neptune Microfloc, Inc.*)

Modules or packs of sloped parallel plates or tube settlers are used to increase the settling area of an existing conventional rectangular or circular clarifier (Fig. 22.16). The additional settling area increases the clarifier influent capacity, while the overflow rate either is reduced or remains constant. The modules are installed in the sedimentation zone of the clarifier and do not project into the clarifier's sludge thickening zone.

Actiflo® Clarifier

The Actiflo clarifier (Fig. 22.17) uses microsand as ballast to add weight to the floc for fast settling. The sand is added to a tank,

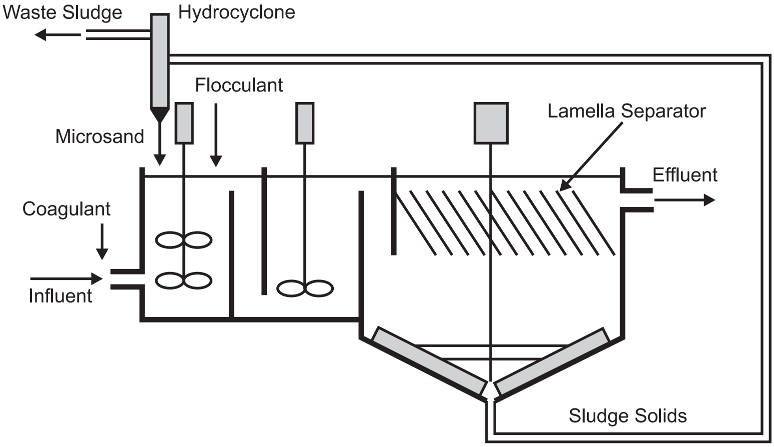


Figure 22.17 An illustration of an Actiflo® clarifier.

where coagulant and effluent are added. The coagulation process occurs on the sand surface, and as the particles increase in size, their weight and settling rate are much higher than without the sand. The clarifier section of the unit is typically a lamella design with inclined plates. Since the rate of fall for the particle is much higher, the velocity of water (rise rate) can be much higher and still achieve excellent water clarity. These clarifiers are equipped with hydrocyclones to separate the microsand from the floc, so the sand can be reused. These clarifiers are often used for effluent treatment, where high flows are desired and physical space is limited. Typical rise rates range from 10 to 20 gpm/ft^2 (24–49 m^3/[h · m^2]), and these rise rates are calculated based on the number of plates in the clarifier.

Densadeg® Clarifier

The Densadeg clarifier (Fig. 22.18) uses extensive mixing and solids contact to build heavy compact floc. There is a coagulation tank with fast mixing followed by a flocculation tank with relatively turbulent mixing. This flocculation tank circulates the water, which then flows up through a center cylinder, and then back down around the outside of the cylinder. Settled floc is returned to this tank to add solids and to increase solids contact. With the extensive mixing, the floc breaks down and reforms into more compact heavier floc. This process is quite compatible with lime softening and effluent treatment applications. The unit is somewhat more chemical demanding than the Actiflo unit, but it does not need microsand or hydrocyclones for operation. Typical rise rates range from 10 to 20 gpm/ft^2 (24–49 m^3/[h · m^2]).

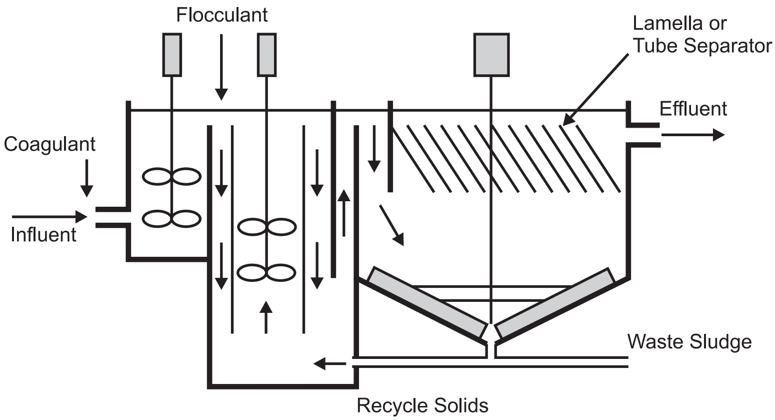


Figure 22.18 An illustration of a Densadeg® clarifier.

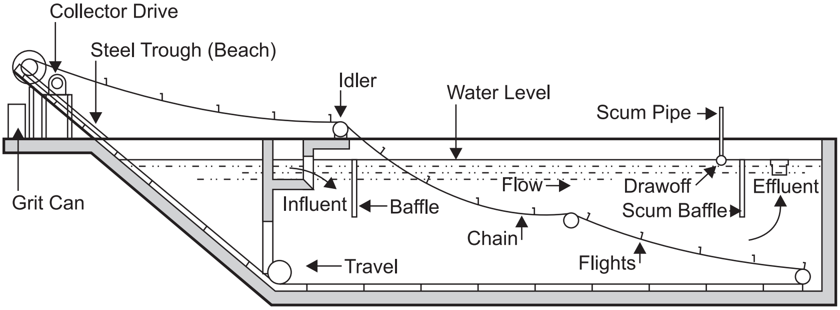


Figure 22.19 Drag tank. (*Courtesy of FMC Corporation*.)

Drag Separator

The rectangular drag tank is a modification of the conventional rectangular clarifier constructed in either a concrete or steel basin. Figure 22.19 illustrates a concrete drag tank. The tank is designed for the removal of dense, anhydrous, gritty solids, such as granulated slag from a foundry cupola or hot strip steel mill scale. Water drains from the solids as they are dragged from the vessel by the flights moving up the beach. The movement of the flights up the beach breaks down fragile solids; hence, the type of solids in the effluent restricts drag tank applications. The detention time in the tank is usually short, limiting flocculation even when chemicals are used and resulting in poor effluent clarity. Chemical flocculation ahead of the tank improves effluent clarity. The flights can be arranged to skim the tank surface to remove floating material such as oil.

Oil/Water Separators

An oil/water separator is used to separate free oil from effluents in refineries, chemical process plants, steel mills, and other industries as primary treatment. These units do not separate soluble impurities, nor do they break oil-in-water emulsions without chemical treatment. Settleable solids settle to the bottom of the basin or to a sludge collection pit. The types of oil/water separators include:

- American Petroleum Institute (API) separator
- Corrugated Plate Interceptor (CPI)
- Tilted Plate Interceptor (TPI) or Parallel Plate Interceptor (PPI)
- Circular oil/water separator

Generally, the free oil/water separator is the first unit in cleaning up an oily effluent before further treatment or reuse. In many cases, an equalization pond is located upstream from the separator. The pond equalizes the effluent flow and characteristics to the separator and through the effluent treatment system, to provide as constant as possible hydraulic and organic loadings on the separator and other processes. Wide variations in the flow to a separator affect the free oil capture efficiency, since the capture is directly related to the hydraulic loading. After the separator, the free oil ideally has been lowered to a level such that the remaining emulsified oil can be removed by DAF or similar device, to protect the following biological treatment process or meet oil discharge requirements.

API Separator

The API separator is a rectangular clarifier with chain and flight oil skimmers (Fig. 22.20), designed in accordance with procedures and specifications developed by the API. API has determined that the design of effluent separators should be based on the rate of rise of oil globules having diameters of 0.15 mm. This globule size, although somewhat arbitrary, has been adopted for design purposes. Both laboratory experiments and a study of existing plant data indicate that satisfactory free oil removal is achieved, when the 0.15 mm diameter particle is used.

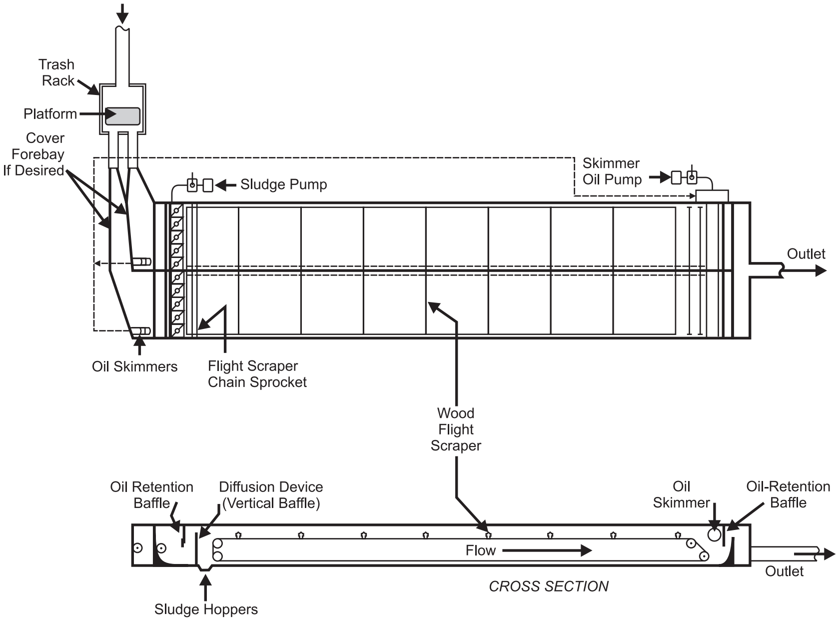


FIGURE 22.20 API separator.

The removal of a given oil globule is a function of the overflow rate (also called the rise rate) in an ideal separator, with no short-circuiting or turbulence. The overflow rate is the influent flow rate divided by the separator's surface area, and has the dimensions of velocity. Any oil globule with a rate of rise equal to or greater than the overflow rate is removed in the separator. This means that any globule having a rate of rise equal to or greater than the water depth divided by the retention time will reach the surface, even though it starts from the bottom of the basin.

The design of an API oil/water separator is based on four relationships:

1. The rise rate of 0.15 mm diameter oil globules is directly related to the difference in the specific gravity of the water and oil, and inversely to the absolute viscosity of the effluent at the design temperature.
2. The minimum horizontal area is based on the oil globule rise rate, corrected by the API factors for turbulence and short-circuiting in the separator.
3. A horizontal water flow not to exceed 15 times the oil globule rise rate or 3 ft/min (0.91 m/min).
4. A minimum water depth to separator width ratio of 0.3. The depth of the separator is to be 3 ft (0.91 m) minimum to 8 ft (2.4 m) maximum. The separator width limits are 6 ft (1.8 m) minimum to 20 ft (6.1 m) maximum. Chain and flight scrapers are limited to a maximum width of 20 ft (6.1 m).

The API standards further recommend, that a minimum of two parallel channels be provided, so that one is available for use when it becomes necessary for the other to be taken out of service for repair or cleaning.

A manually rotatable, slotted pipe skimmer is typically used for removal of the oil. Some installations use a rotating drum skimmer that can be either fixed or floating. The drum skimmer picks up a thin film of oil as it rotates, which is scraped off and drained into a collection sump. The drum can be made of carbon steel, stainless steel, aluminum, or plastic depending on the manufacturer. Optimum rotational speed is 0.5 to 1.5 ft/s (0.15–0.46 m/s) with a drum submergence of 0.5 inches (13 mm) or greater.

Corrugated Plate Interceptor

The CPI (Fig. 22.21) contains corrugated plates that are 0.75 to 2 inches (19–51 mm) apart, and at an angle of approximately 45° from vertical. Free oil globules rise only until contacting a corrugated plate, coalesce into larger drops with other globules, rise to the top of the plate pack,

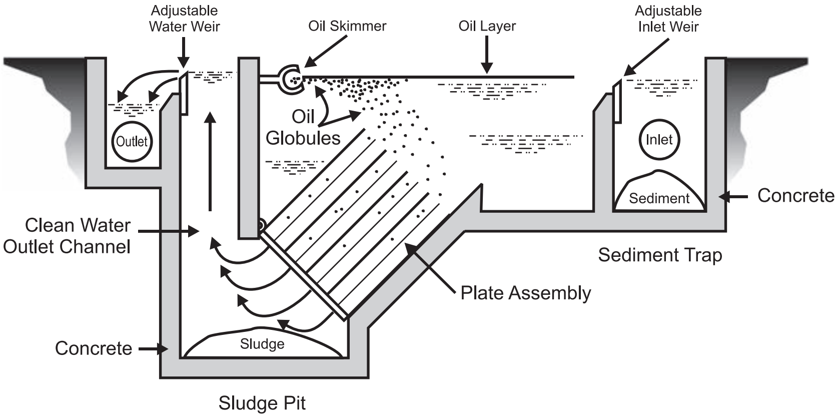


Figure 22.21 Corrugated plate interceptor.

and finally to the water surface where they are skimmed off. The CPI maintains laminar flow conditions, while decreasing the distance that oil globules must rise to be collected, with an overall reduction of space taken by the oil/water separator. Settleable solids settle to the surface of the plates and drop down to the sludge pit.

The capacity of a CPI is based on the same free oil globule rise rate and hydraulic overflow principles as the API separator. In this case, the horizontal projected area of the corrugated plates, are used for the horizontal area in the API procedure.

Parallel Plate Interceptor

The PPI is similar to a plate clarifier. It is not extensively used in the refining or petrochemical industry, since the corrugated plates in the CPI are more efficient in coalescing free oil. However, PPI is used in other industries. The PPI operates on the same principles as the CPI.

Circular Oil/Water Separator

The design of circular oil/water separators follows the arrangement of conventional circular clarifiers with a central influent entrance, a discharge on the periphery, and includes sludge rakes and oil skimming. The sizing of the unit is the same as the API separator, since the circular arrangement provides a horizontal effluent flow, free oil globules rising, and suspended matter settling. A diagram of a circular oil/water separator is shown in Fig. 22.22. The larger clarifier handles the oily effluent, while the smaller is a primary clarifier for effluent that does not contain any oil.

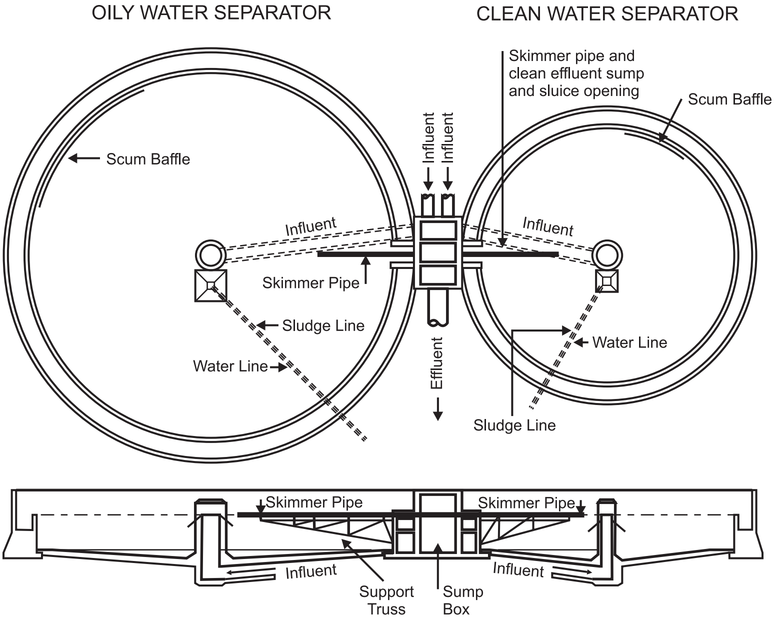


Figure 22.22 Circular oil/water separator.

Flotation Clarification

The DAF clarification process is used to separate suspended solids or liquors from water that are lighter than or only slightly heavier than water. These wastes include oils, fats, greases, fibers, biosolids (thickening and secondary clarification in biological treatment plants), algae, and metal hydroxides to name a few. DAF is therefore used in many industries such as oil refining, petrochemical, chemical, steel, meat and poultry packing, vegetable processing, pulp and paper, railroad terminals, and the prepared food industry. In these industries, oily waste may coat solid particles, giving them a tendency to float rather than settle. An API separator may precede the DAF system for the removal of free oil in many applications.

The flotation process consists of attaching fine gas bubbles (10–100 μm) to suspended solids or oily material, which reduces the specific gravity of the solids. The fine bubbles are produced by dissolving gas into the water at elevated pressure, followed by the subsequent reduction back to atmospheric pressure. The dissolved gas (in excess of atmospheric saturation) is released as fine bubbles, when the pressure is reduced. Air is commonly used as the gas, but other gases such as nitrogen are used, depending on the application. Nitrogen is used in applications where there is a possibility of explosion, such as refineries.

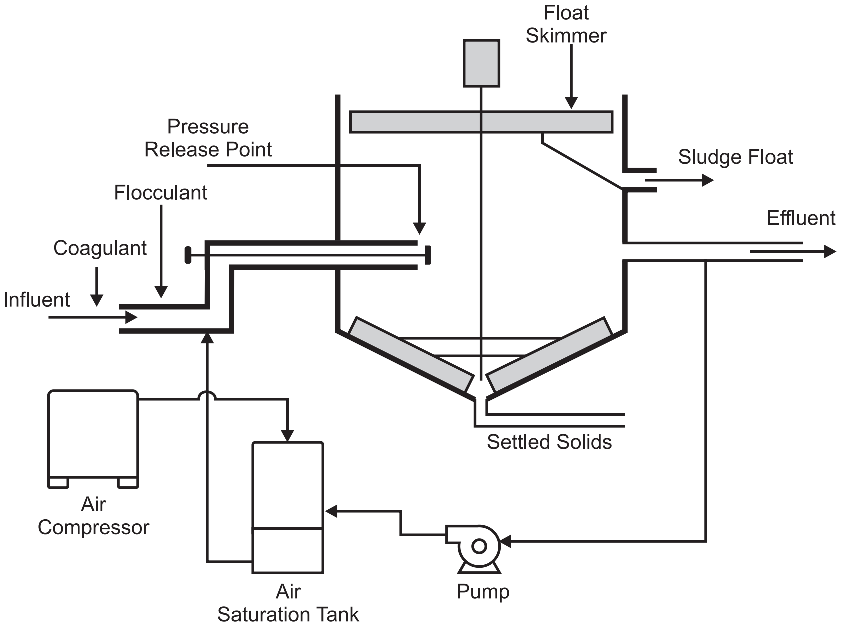


FIGURE 22.23 Dissolved air flotation system.

The Dissolved Air Flotation System

A schematic flow diagram of a typical DAF unit is illustrated in Fig. 22.23. Part of the effluent is saturated with air at the elevated pressure in the air saturation tank and recycled to the influent. The backpressure valve (also referred to as the pressure relief valve) at the indicated pressure release point in the flotation cell, reduces the pressure on the recycle flow where it mixes with the influent. The backpressure valve is located external to the flotation cell in other designs. In this case, the influent is mixed with the recycle flow after the pressure relief valve outside of the flotation cell. The excess dissolved air then comes out of solution, since the flow is now at atmospheric pressure, and the small gas bubbles attach to the particles in the effluent and rise to the surface of the cell. The floated material is skimmed off the cell for further handling or recovery. The clarified effluent is discharged, reclaimed, or receives further treatment, depending on discharge requirements. The flotation cell can be either circular or rectangular. The circular unit is more economical for larger flows.

An organic flocculant or coagulant plus a flocculant are used in many instances to improve the solids capture or break oil emulsions. As in gravity settling, the coagulant can be an inorganic, such as an iron or aluminum salt, organic polymer, or a blend of inorganic and

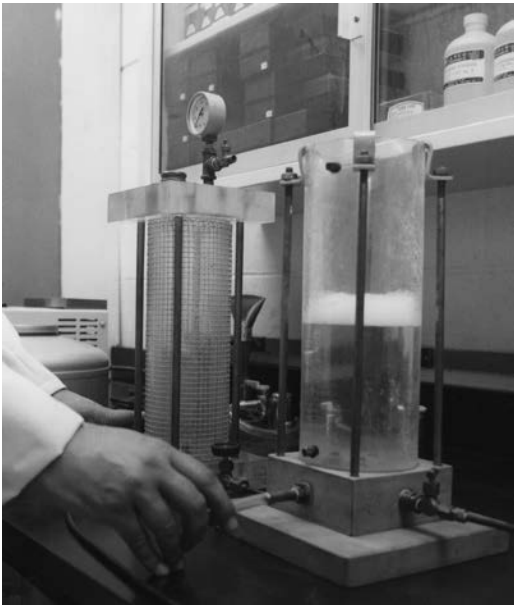


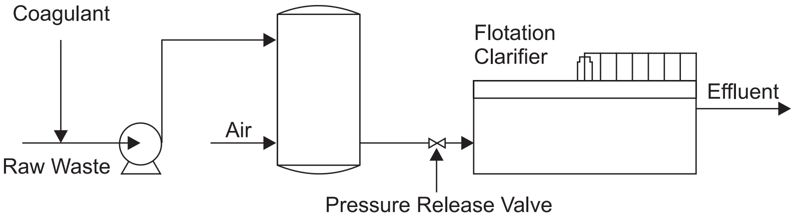
FIGURE 22.24 Bench DAF test. (*Courtesy of Infilco Degremont Inc.*)

organic. Anionic, cationic, or nonionic organic flocculants may be used depending on the effluent. Cationic flocculants are most commonly used, since the small air bubbles have a slightly negative charge. A bench DAF column test (Fig. 22.24) can be used to simulate the clarification process and evaluate various chemical programs. The typical addition points for the chemicals are indicated in Fig. 22.23.

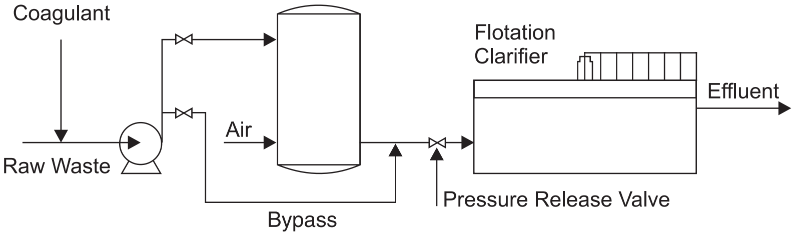
Types of DAF Systems

The three different types of DAF systems are referred to as total pressurization, partial pressurization, and recycle pressurization. In total pressurization, the entire waste stream is pressurized and saturated with air (Fig. 22.25a). The material to be separated must be able to withstand the shearing forces in the pressure pump, air saturation tank, and backpressure valve, or the floc must be capable of quickly reforming after the pressure is released. In addition, the material in the effluent may plug the air saturation tank and backpressure valve, depending on the quantity and size of material. This method is not used for oily or greasy wastes, as they can be mechanically emulsified.

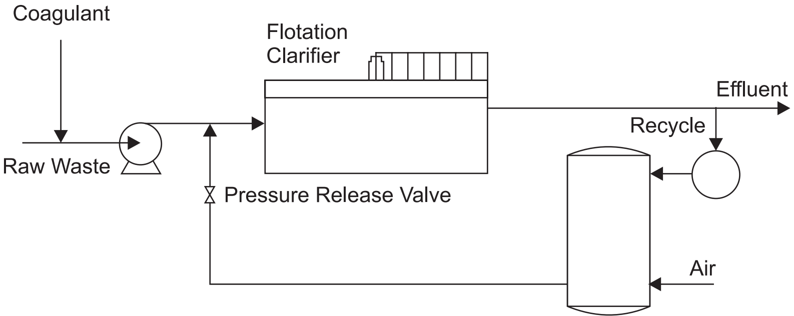
Only a portion of the influent is pressurized in partial pressurization (Fig. 22.25b). This method reduces pumping costs but has the same performance problems as indicated for total pressurization.



(a) Total aeration of raw waste



(b) Partial aeration of raw waste



(c) Aeration of recycle

Figure 22.25 Types of DAF systems.

In recycle pressurization, (Fig. 22.25c) a side stream (recycled effluent) of clarified water is pressurized, saturated with air, and then mixed with the chemically pretreated waste stream. The pretreatment may be in a separate flocculation tank or in-line, depending on the application. This method is preferred when the effluent must be pretreated with chemicals, to eliminate shearing of the floc and eliminate plugging of the pressurization system. This is the preferred method to produce a low suspended solids effluent, even though the recycle flow increases the size of the flotation cell. Most systems today use recycled pressurization.

Operating Parameters

The hydraulic loading, expressed as gpm/ft^2 (m^3/[h·m^2]) of flotation area, typically controls the capacity of a DAF cell for clarification applications. The solids loading or flux, expressed as lb/[h·ft^2] (kg/[h·m^2]), may be the limiting factor, when the TSS are greater than about 1000 mg/L. The flotation effect is established by the recycle ratio and the air/solids ratio.

Hydraulic Loading Rate

The hydraulic loading rate (also referred to as rise rate or overflow rate) is one of the important considerations, since the degree of clarification efficiency is a function of the hydraulic loading. The loading rate is normally in the range of 1.5 to 2 gpm/ft^2 (3.7–4.9 m^3/[h·m^2]) including recycle. The higher loading is for "easy to float" material such as oil and grease, while the lower number is for "slow floating" material such as biosolids and algae. Generally, a rise rate greater than 2 gpm/ft^2 (4.9 m^3/[h·m^2]) results in higher effluent suspended solids. An exception is DAF systems floating fiber, such as white water clarification in paper mills, which are designed for 2.5 gpm/ft^2 (6.1 m^3/[h·m^2). These loading rates typically capture 80 to 85% of the suspended solids without chemical treatment, and 90 to 95% plus with chemical treatment. Chemical treatment is necessary to resolve oil and fat emulsions to obtain removal of these emulsified materials.

The hydraulic loading rate can be calculated using Eq. (22.5):

$$\mathrm{HLR} = \frac{(F_i + F_r)}{A} \tag{22.5}$$

where HLR = hydraulic loading rate, gpm/ft^2 (m^3/[h·m^2])
F_i = influent flow, gpm (m^3/h)
F_r = recycle flow, gpm (m^3/h)
A = net flotation area inside flotation baffles, ft^2 (m^2)

Some DAF cells have plate packs like parallel plate clarifiers to reduce the flotation cell floor space. The flotation cell hydraulic loading rate in this case is on the horizontal projected area of the plates, just like with plate clarifiers. The hydraulic loading rates previously discussed, are also used on the projected horizontal area in this case. Care must be taken to ensure that the loading rate is calculated on the floor space area and not the projected plate area.

Solids Loading Rate

The capacity for DAF clarification applications is typically controlled by the hydraulic loading rate. The solids loading rate determines the DAF capacity for clarification, when the influent solids exceed approximately 1000 mg/L and for biological solids thickening. Solids loading is calculated by dividing the influent TSS by the net flotation area. The solids in the recycle flow are customarily ignored in this calculation. The actual solids loading rate for clarification applications needs to be periodically checked using the following:

US Units

$$\mathrm{SLR} = \frac{(F_i)(\mathrm{TSS})}{(2000)(A)} \tag{22.6}$$

where SLR = solids loading rate, lb/[h · ft^2]
F_i = influent flow rate, gpm
TSS = total suspended solids, mg/L
A = net flotation area inside flotation baffles, ft^2
The 2000 factor = (694 gpm/mgd)(24 h/d)/8.33 lb/gal.

Metric Units

$$\mathrm{SLR} = \frac{(F_i)(\mathrm{TSS})}{(1000)(A)} \tag{22.7}$$

where SLR = solids loading rate, kg/[h · m^2]
F_i = influent flow rate, m^3/h
TSS = total suspended solids, mg/L
A = net flotation area inside flotation baffles, m^2
The 1000 factor = (10^6 mg/kg)(1 m^3/1000 L).

Typical solids loading rates are 1.5 lb/[h · ft^2] (7.3 kg/[h · m^2]) without chemicals and 2 lb/[h · ft^2] (9.8 kg/[h · m^2]) with chemical treatment. A polymer can be used to increase the solids loading rate to achieve the same solids capture or improve the solids capture efficiency at lower loading rate.

Air/Solids Ratio

The performance of a flotation system depends on having sufficient air bubbles present to make contact with the suspended solids and float them. An insufficient quantity of air results in only partial flotation and poor clarification. On the other hand, excessive amounts of air can cause turbulence and high surface velocity, which can lead to short-circuiting and high effluent suspended solids. The performance of a flotation unit in terms of effluent quality and float solids concentration is related to an air/solids ratio, defined as pound (kilogram) air per pound (kilogram) dry suspended solids. The ratio is calculated from operating data using Eq. (22.8):

$$A/S = \frac{1.3(\mathrm{Air})(\mathrm{ERT})(F_r)}{(\mathrm{TSS})(F)} \tag{22.8}$$

where A/S = air/solids ratio, lb/lb (kg/kg)
Air = air solubility at operating conditions, mL/L
ERT = saturation tank (pressurization tank) efficiency, decimal
F_r = recycle flow rate, gpm (m^3/h)

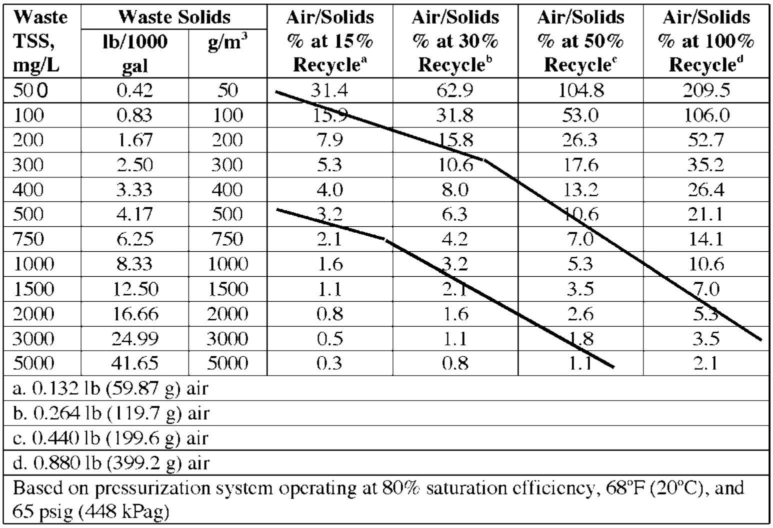
TSS = total influent suspended solids, mg/L
F = influent flow rate, gpm (m^3/h)
1.3 = approximates the density of air at ambient temperature, mg/cm^3

The air saturation tank dissolving efficiency (ERT) is in the range of 0.5 to 0.8 for clean water depending on the manufacturer.

Recycle Ratio

In DAF clarification, the term recycle, expressed in percent of total influent flow, has been historically used instead of the air/solids ratio, even though the air/solids ratio is critical to the clarification process. Normally, the necessary air/solids ratio in clarification processes is considerably higher that what is used in DAF thickening. The main consideration in clarification is to provide a sufficient quantity of air bubbles to find and contact the suspended solids. Statistically, more air bubbles are needed to contact the considerably lower influent suspended solids concentration in clarification of dilute suspensions, as opposed to thickening applications. This low influent suspended solids concentration is the reason for the higher air/solids ratio.

Figure 22.26 gives a general picture of the recycle rate requirement, based on the TSS in the effluent. This figure was compiled from several DAF units treating a variety of effluents including oil, fiber, fat, grease, latex, and others in a diversity of industries. The area between the operational range lines gives a choice of two recycle



Waste TSS, mg/L	Waste Solids		Air/Solids % at 15% Recycle[a]	Air/Solids % at 30% Recycle[b]	Air/Solids % at 50% Recycle[c]	Air/Solids % at 100% Recycle[d]
	lb/1000 gal	g/m^3				
500	0.42	50	31.4	62.9	104.8	209.5
100	0.83	100	15.9	31.8	53.0	106.0
200	1.67	200	7.9	15.8	26.3	52.7
300	2.50	300	5.3	10.6	17.6	35.2
400	3.33	400	4.0	8.0	13.2	26.4
500	4.17	500	3.2	6.3	10.6	21.1
750	6.25	750	2.1	4.2	7.0	14.1
1000	8.33	1000	1.6	3.2	5.3	10.6
1500	12.50	1500	1.1	2.1	3.5	7.0
2000	16.66	2000	0.8	1.6	2.6	5.3
3000	24.99	3000	0.5	1.1	1.8	3.5
5000	41.65	5000	0.3	0.8	1.1	2.1

a. 0.132 lb (59.87 g) air

b. 0.264 lb (119.7 g) air

c. 0.440 lb (199.6 g) air

d. 0.880 lb (399.2 g) air

Based on pressurization system operating at 80% saturation efficiency, 68°F (20°C), and 65 psig (448 kPag)

FIGURE 22.26 Suggested recycle rates for DAF clarification process based on waste TSS.

rates; the lower recycle rate is selected for an "easy to float" material, and the higher rate for a "slow floating material." A recycle rate of 30 to 50% is generally used, if the influent TSS are unknown, depending on how hard or easy the material is to float.

Generally, effluents containing oils, fats, greases, fibers, and other lighter than water solids are classified as easy to float. Types of slow floating materials are biosolids, metal hydroxides, algae, and granular media solids.

Pressurization Systems

Figure 22.27 is a diagram of a typical pressurization system for a DAF system. The operating pressure of the system just upstream from the pressure relief (backpressure) valve is generally 60 to 70 psig (414–483 kPag), although there are a few manufactures that design their systems for 40 to 45 psig (276–310 kPag). The system should be operated at the manufacture's design operating pressure, as any changes in pressure result in changes in recycle flow, hydraulic loading, saturation tank retention time, air dissolving efficiency, and quantity of air dissolved.

The internals of the saturation tank are designed to break the recycle water into small droplets, to maximize the water surface area and thus the transfer rate of the gas into the liquid. The internals vary depending on the manufacturer, and can be spray nozzles (Fig. 22.28), packing similar to a high-rate cooling tower, spray jet with a splash plate, and various baffle configurations. All of these designs require a gas atmosphere above the liquid level in the tank.

The liquid level in the saturation tank is controlled in one of two ways. The first, referred to as the bleed-off system, continuously feeds

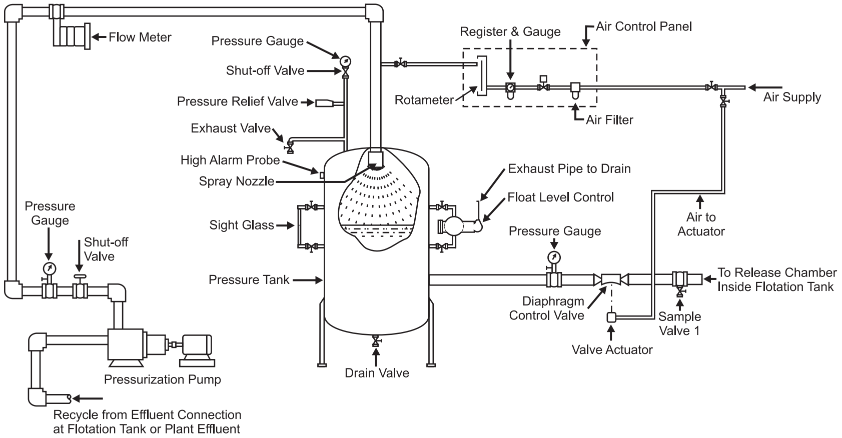


Figure 22.27 Typical pressurization system.

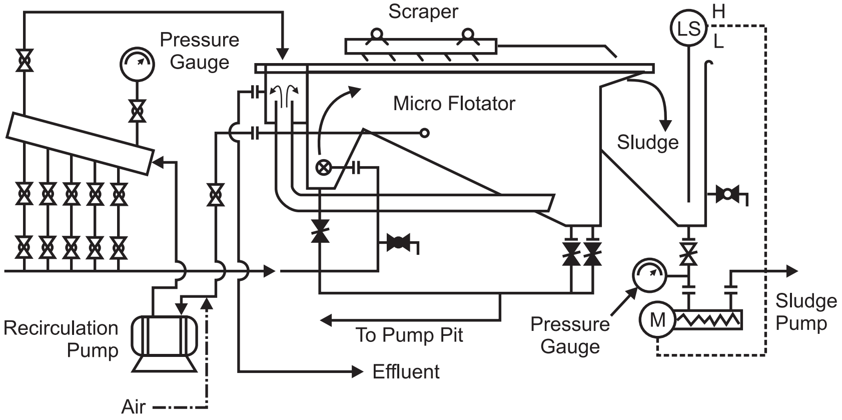


Figure 22.28 DAF system without air saturation tank.

air to the tank. A level control valve (Fig. 22.29) opens with decreasing water surface, to vent air that has not gone into solution, and returns the water surface to its design elevation. The second is called the on/off feed air system in that the air to the tank is turned on/off in response to the rising/falling of the water surface in the tank.

Losing the water level surface control by flooding the tank with air or water, due to too much or too little air addition, or failure of the automatic level control system, are common causes for failure of the flotation process. Flooding the tank with air results in poor dissolving efficiency and the presence of "geyser" eruptions on the surface of the flotation cell, due to the free air being introduced into the cell. Flooding the tank with water results in the destruction of the water droplet production in the tank and the loss of air dissolving efficiency.

Some DAF designs do not use an air saturation tank (Fig. 22.28). Instead, a centrifugal pump that is specially designed to handle air-

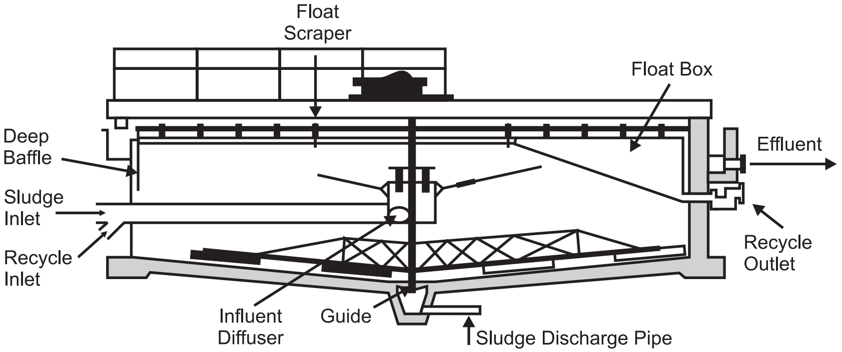


Figure 22.29 Circular flotation cell.

in-water solutions is used. The pump is capable of handling up to 35% entrained air without air binding, and produces air bubbles down to 30 μm. The design in Fig. 22.28 uses a slanted tube to vent excess air and several backpressure valves to release the system pressure. This type of system is used in easier to float applications, such as poultry packing effluent.

A milky white water in the flotation cell indicates that the pressurization system is functioning properly. High dissolved solids or antifoams in the effluent can adversely affect air solubility, reducing the amount of small air bubbles available for flotation.

Flotation Cell

The circular flotation cell or tank is similar to a circular clarifier having surface skimmers and sludge rakes or plows (Fig. 22.29). The number of skimmers provided is based on the anticipated float quantity. The influent is introduced at about mid-depth in a horizontal direction to prevent the flow from boiling in the center of the tank. A deep flotation baffle is provided around the periphery, so that the clarified water must flow downward from the inlet to the effluent weirs, while the floating material rises.

Another type of circular flotation cell is called the shallow tank configuration (Fig. 22.30), since the side water depth of the tank is only about 2.5 ft (0.76 m), while the more conventional circular cell (Fig. 22.29) has a tank side water depth of 6 to 8 ft (1.8–2.4 m). The influent feed containing the recycle flow, is introduced into the tank from a rotating, radial manifold. The rotational velocity of the manifold is opposite to, and set equal to, the influent water velocity. The influent is thus introduced into the tank at essentially zero velocity. This in

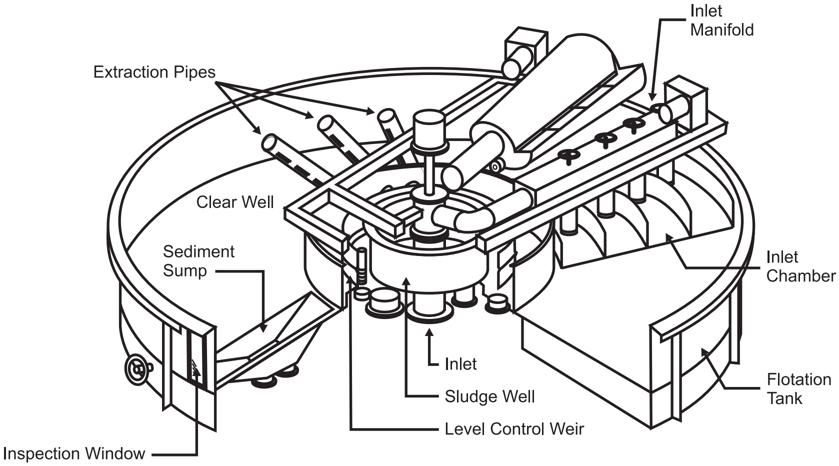


FIGURE 22.30 Shallow tank flotation cell.

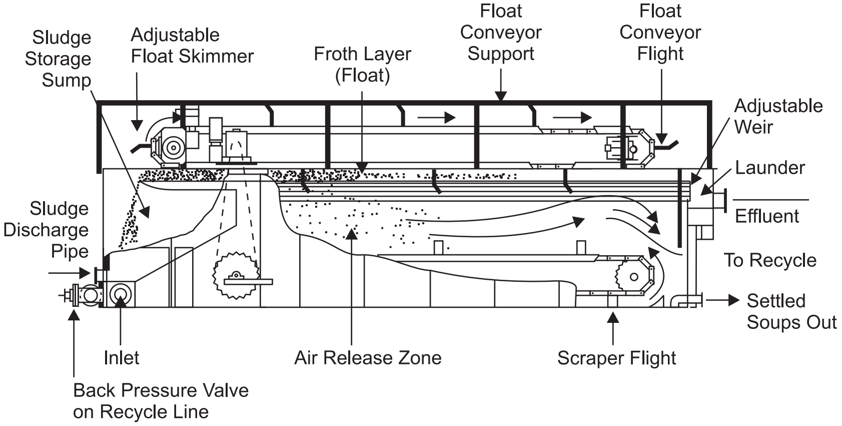


FIGURE 22.31 Rectangular flotation cell.

essence static condition allows efficient flotation in the shallow tank, leaving the clarified water in the lower stratum of the tank, from where it is removed by the effluent extraction pipes attached to the rotating carriage. The rotating scoop attached to the carriage lifts the floated solids from the surface and transports them to the center of the unit, from where they are discharged from the tank. This type of unit is commonly used in the pulp and paper industry.

A rectangular flotation cell may be equipped with a chain and flight scraper for the floated material, and a second chain and flight scraper for the settled sludge (Fig. 22.31). Depending on the application, only a scraper for the float may be provided, in which case the floor of the basin may be sloped to hoppers. A reciprocating float scraper mechanism in place of the chain and flight type is used in some designs. The float is scraped to a sump at the feed end of the basin. An adjustable effluent overflow weir is provided, following a deep float containment baffle.

Float Removal Control

Most DAF units are equipped with adjustable overflow effluent weirs that determine the operating water level in the unit. Consequently, the weirs control how deep or shallow the skimmer blades dip into the floated solids. The water level rises as the overflow weir is raised, permitting the skimmer blades to dip more deeply into the floated material. This results in a greater percent of the floated material being removed with each pass of the skimmer. This in turn normally results in a cleaner effluent but a wetter (lower percent solids) float. Lowering the weir has the opposite effect. The solids get dryer (higher percent solids), but the effluent quality may deteriorate.

Float skimmer blades remove the floated material from the top of the flotation unit. The skimmers may be driven by variable speed motors, which operate continuously, or by constant speed motors, operating intermittently on a timer. In either case, the mechanism needs to be adjusted to remove the float at the rate dictated by the treatment goals.

Generally, the slower (run less frequently) the skimmers move, the drier the float removed, but deterioration of the effluent water quality may result. Increasing the speed of the skimmers (run more frequently) results in more total solids being removed, which may improve the effluent quality at the expense of a wetter float.

Plant Flows

Minimum, maximum, and average flows must be considered and provisions made to cope with surges. A DAF clarifier is hydraulically capable of processing a higher flow rate with a constant recycle rate for brief or infrequent surges in plant flow, but the effluent quality may suffer. An equalization basin ahead of the DAF system is best for eliminating large, regular variations in effluent, so that the system can be operated at as constant a flow as possible. Generally, reducing overflow rates below 1 gpm/ft^2 (2.4 m^3/[h · m^2]) does not measurably improve suspended solids capture.

Induced Air Flotation (IAF)

Mechanically entraining air and dispersing it through the liquid as fine bubbles, in contrast to the release of dissolved gas from solution, is also used to achieve flotation. A rectangular tank is divided into four flotation cells. Each cell is equipped with either a motor-driven aerating rotor mechanism, or an aspirating nozzle. (Fig. 22.32 illustrates the

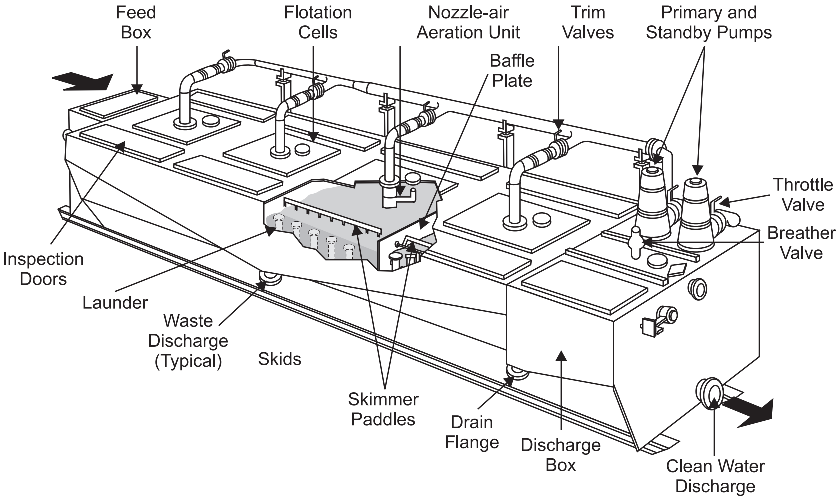


FIGURE 22.32 Nozzle-type-induced air flotation. (*Courtesy of Wemco Division, Envirotech Corporation*.)

nozzle arrangement.) The specially designed rotor mechanism or nozzle draws air into the cell and disperses it throughout the cell. Oil globules and fine suspended solids attach to the bubbles as they rise to the surface, from where they are removed by skimmer paddles.

The induced air flotation system is primarily used to remove oil from effluents with or without the addition of chemicals. It cannot handle effluents that contain heavy, settleable solids that will not float, since the unit does not have any capabilities for removing settled sludge.

CHAPTER 23

Secondary Effluent Treatment

Secondary effluent treatment systems are biological systems with the purpose of processing primary effluent system effluent. The main goal of secondary effluent treatment is to remove soluble pollutants from effluent. During secondary effluent treatment, consideration must be given to handling of sludge, where microbial organisms under proper environmental conditions perform an effluent decontamination function. Descriptions of the major types of secondary effluent processes are presented, accompanied by equations for the chemistry involved and information on equipment design and performance parameters.

General Principles of Secondary Treatment

Secondary treatment processes in the overall waste treatment system have three major purposes:

1. Biological oxidization of soluble organic matter that remains after primary treatment
2. Absorption of suspended solids carried over from primary treatment as well as settling of solids generated as a result of the biological process
3. Biological removal of certain nutrients like ammonia, nitrate, and phosphorus that are dissolved in effluent

Secondary biological treatment requires availability of many microorganisms (bacteria), good contact between these organisms and organic material, availability of oxygen, sufficient nutrients, favorable temperature conditions, favorable pH ranges, and adequate time for organisms to work. Microorganisms in secondary treatment systems need a source of food or energy [biochemical oxygen demand (BOD)], time (the biological process retention time), and a source of oxygen to function effectively and efficiently.

Secondary or biological waste treatment processes can be classified by the presence or absence of dissolved oxygen (DO). Terms usually applied to this classification are:

- Aerobic—Usually DO is maintained higher than 0.5 mg/L. Optimum is 1–2 mg/L or slightly higher in specific cases.
- Anoxic—DO should be less than 0.5 mg/L and most preferably nondetectable. Combined oxygen such as nitrate and nitrite can be presented.
- Anaerobic—DO should be nondetectable and no nitrate or nitrite source exists.

Biological treatment processes can also be classified according to their means of providing medium for the biological organisms growth:

- Attached growth—a mass of individual microorganisms attaching themselves to a fixed media (e.g., plastic rings) in a slime film (sometimes called fixed film)
- Suspended or slurry growth—a process where microorganisms are kept in a suspended state, as individual organisms, or as a mass of organisms (sludge flocs) that are mixed with the effluent being treated in a solids suspension termed mixed liquor

In modern waste treatment facility designs, there are usually two common components of a typical waste treatment system:

1. A biological reactor or vessel, in which effluent comes in contact with the microbial population
2. A clarifier, in which biological solids are settled and collected in the sludge blanket and thereby separated from clarified effluent, which passes to the receiving waters

Table 23.1 shows the major biological treatment processes used for different treatment.

Basic Methods of Secondary Treatment

Secondary effluent treatment methods include activated sludge, aerated lagoons, trickling filters, and rotating biological contactors.

Activated Sludge

The activated sludge process is a suspended growth biological effluent treatment technique, in which a mixture of effluent and biological mass (microorganisms) is agitated and aerated. The biological

Type	**Common Name**	**Use***
	Aerobic Processes	
Suspended growth	Activated sludge:	
	Conventional (plug flow) Continuous flow stirred tank Step aeration Pure oxygen Modified aeration Contact stabilization Extended aeration Oxidation ditch	Carbonaceous BOD removal (nitrification)
	Suspended growth nitrification	Nitrification
	Aerated lagoon	Carbonaceous BOD removal (nitrification)
	Aerobic digestion:	
	Conventional air	Stabilization
	Pure oxygen	Carbonaceous BOD removal
	High-rate aerobic algal pond	Carbonaceous BOD removal
Attached growth	Trickling filter:	
	Low rate High rate	Carbonaceous BOD removal (nitrification)
	Roughing filter	Carbonaceous BOD removal
	Rotating biological contactor (RBC)	Carbonaceous BOD removal (nitrification)
	Packed bed reactor	Nitrification
Combined processes	Trickling filter, activated sludge Activated sludge, trickling filter	Carbonaceous BOD removal (nitrification)
	Anoxic Processes	
Suspended growth	Denitrification	Denitrification
Attached growth	Denitrification	Denitrification

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*Major use is presented first; other uses are shown in parentheses.

TABLE 23.1 Major Biological Processes Used for Effluent Treatment

Type	Common Name	Use*
Anaerobic Processes		
Suspended growth	Anaerobic digestion:	
	Standard rate single stage High rate single stage Two stage	Stabilization, carbonaceous BOD removal
	Anaerobic contact process	Carbonaceous BOD removal
Attached growth	Anaerobic filter	Carbonaceous BOD removal, stabilization (denitrification)
	Anaerobic lagoon (pond)	Carbonaceous BOD removal, stabilization
Aerobic/Anoxic or Anaerobic Processes		
Suspended growth	Single stage	Carbonaceous BOD removal, nitrification, denitrification
Attached growth	Nitrification/denitrification	Nitrification/denitrification
Combined processes	Facultative lagoon (pond)	Carbonaceous BOD removal
	Maturation or tertiary pond	Carbonaceous BOD removal (nitrification)
	Anaerobic-facultative lagoon	Carbonaceous BOD removal
	Anaerobic-facultative-aerobic lagoon	Carbonaceous BOD removal

Table 23.1 Major Biological Processes Used for Effluent Treatment (*Continued*)

mass is subsequently separated from treated effluent in a clarifier, and returned to the aeration process to maintain a balance of biological solids and effluent being treated. The activated sludge process derives its name from the biological mass formed when air is continuously injected into nutrient-rich effluent. Microorganisms are mixed thoroughly with organics under conditions that stimulate use of organics as a food source. As microorganisms grow, multiply, and mix by agitation with air, individual organisms clump together (flocculate), to form an active mass of microbes called activated sludge. Variations of the activated sludge process are discussed in a later section.

Aerated Lagoon

An aerated lagoon is a basin in which effluent is treated on a flow-through basis. Oxygen is usually supplied by surface aerators or submerged aeration devices.

Trickling Filter

The trickling filter process is a fixed-film biological process that uses slag, rock, stones, plastic, or wood as medium on which microorganisms grow. Effluent is typically applied as a spray from moving distributors. As effluent trickles through the bed, microorganisms grow on the surface of the packing in a fixed film. Effluent passes over and through the medium to provide needed contact between microorganisms and organics. Biological growth sloughs off the medium when the inner biological area can no longer receive oxygen. A clarifier is used after the trickling filter to remove this biological material before discharging treated water. Sometimes, effluent from the clarifier is recycled back to the trickling filter to increase BOD removal efficiency, and maintain optimum hydraulic loading on the filter.

Rotating Biological Contactor

This process is a fixed-film biological process that uses rotating discs mounted on shafts and placed in a tank, with about 40% of the disc area immersed in the tank (effluent) and the remainder exposed to the atmosphere. A biological film or biomass grows on the surface of the discs. Rotation brings biomass in contact with effluent for removal of organics and with the atmosphere for absorption of oxygen. A secondary clarifier collects excess solids that are produced on the biodiscs.

Principles of Biological Waste Treatment

In the biological treatment of effluents, a mixed population of microorganisms uses colloidal and dissolved organics found in effluent from primary treatment as its main food supply. In consuming these organics, microorganisms use part of the organic substances to obtain energy needed for their life activities.

Biological respiration, in the presence of DO, produces products such as carbon dioxide, water, sulfates, nitrates, and phosphates. The remaining part of consumed organics is used as building blocks in a series of synthesis (reproduction) reactions, which result in an increased microorganism population (cell growth). Therefore, colloidal and dissolved organics originally present in effluent are transformed partly into a stable form, such as carbon dioxide, and partly into a viable biological mass. This biochemical reaction is active in all biological treatment processes.

The biological mass is subsequently separated from the effluent in secondary clarifiers, to ensure a proper degree of treatment within effluent and water quality standards.

Important Microorganisms

In the activated sludge process, microorganisms are dispersed throughout the water phase; in trickling filters, RBCs, and other fixed-film processes, microorganisms are attached to a fixed surface, forming a biological film. In either process, microorganisms are doing the work, and therefore, all precautions must be taken to assure a favorable environment for them.

Microorganisms considered important in biological treatment are: bacteria, fungi, algae, protozoa, rotifers, and worms.

Bacteria

Bacteria are single-cell microorganisms. They use soluble food and, in general, are found wherever moisture and a food source are available. Their usual mode of reproduction is by binary fission (i.e., by dividing, the original cell becomes two new organisms), although some species reproduce sexually or by budding. Even though there are thousands of different species of bacteria, their general form falls into one of three categories: spherical, cylindrical, and helical. Bacteria vary widely in size. Representative sizes are 0.5 to 1.0 μm in diameter for the spherical, 0.5 to 1.0 μm in width by 1.5 to 3.0 μm in length for the cylindrical (rods), and 0.5 to 5 μm in width by 6 to 15 μm in length for the helical (spiral).

In general, two types of bacteria can be distinguished: floc forming and filament forming. Floc-forming bacteria have the capability, under the right conditions, to clump together using excreted exocellular polymer to form a floc that is large and heavy enough to settle. Filament-forming bacteria also remove organics from effluent but are characterized by stringy or threadlike forms that are extremely light and easily washed out from the clarifier. It is clear that floc formers are preferred in a biological treatment plant. The character and type of effluent as well as the environment (regime in which they live) dictate which forms will be the majority.

Temperature and pH play a vital role in the life and death of bacteria. The rate of reaction for microorganisms increases with increasing temperature, doubling with about every 18°F (10°C) of temperature rise, until some limiting temperature is reached. According to the temperature range in which they function best, bacteria may be classified as cryophilic (psychrophilic), mesophilic, or thermophilic. Typical temperature ranges for bacteria in each of these categories are presented in Table 23.2.

	Temperature, °C	
Type	**Range**	**Optimum**
Cryophilic*	10–30	12–18
Mesophilic	20–45	25–40
Thermophilic	45–75	55–65

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*Also called psychrophilic.

Table 23.2 Typical Temperature Ranges for Various Bacteria

The vast majority of secondary treatment plants is designed for mesophilic organisms and needs to be operated in the 25 to 40°C range for best treatment.

The pH of a solution is also a key factor in the growth of organisms. Most organisms cannot tolerate pH levels above 9.5 or below 4.0. Generally, optimum pH for bacteria growth lies between 6.5 and 7.5.

Fungi

In biological treatment systems, fungi are considered multicellular, nonphotosynthetic, and heterotrophic organisms.

Most fungi are strict aerobes. They have the ability to grow under low moisture conditions and can tolerate an environment with relatively low pH. Optimum pH for most species is 5.6; the range is 2 to 9. Fungi have a low nitrogen requirement, needing only approximately one-half as much as bacteria.

The ability of fungi to survive under low pH and nitrogen conditions makes them very important in the biological treatment of some industrial wastes.

Algae

Algae are unicellular or multicellular, autotrophic, and photosynthetic organisms. In oxidation ponds, algae are valuable in that they have the ability to produce oxygen through photosynthesis. At night, when light is no longer available for photosynthesis, algae consume oxygen in respiration, producing carbon dioxide (CO_2). Oxygen is also consumed by biological decomposition of dead algae. (High die off of algae results in stagnant ponds with their associated odors.) Respiration also occurs in the presence of sunlight; however, the net reaction is production of oxygen. Equations 23.1 and 23.2 represent simplified biochemical reactions for photosynthesis and respiration:

Photosynthesis:

$$CO_2 + 2H_2O + \text{light} \rightarrow CH_2O + O_2 + H_2O \tag{23.1}$$

CH_2O represents new algae cells.

Respiration:

$$CH_2O + O_2 \rightarrow CO_2 + H_2O \tag{23.2}$$

In an aquatic environment, it can be seen that this type of metabolic system produces a diurnal variation in DO. The ability of algae to produce oxygen is vital to the ecology of the water environment. In some types of biological treatment (oxidation pond), algae are needed to supply oxygen to aerobic, heterotrophic bacteria.

Algae are also considered a nuisance in waste treatment. Algae cells may form large floating mats that reduce the oxygen transfer ability of a treatment tank or clog filters. The die off of large quantities of algae at night depletes DO, and the pond becomes odorous due to anaerobic decomposition of dead algae. They also cause an increase in effluent total suspended solids (TSS) levels from lagoon systems or activated sludge clarifiers, particularly during summer months.

Protozoa

Protozoa are motile, microscopic organisms that are usually single cells. The majority of protozoa are aerobic heterotrophs, although a few are anaerobic. Protozoa are generally an order of magnitude larger than bacteria and often consume bacteria as an energy source. In effect, protozoa act as polishers of effluents from biological waste treatment processes by consuming free swimming bacteria and particulate organic matter.

Ciliata Movement by means of cilia is characteristic of these protozoa. Cilia are hair-like extensions from the cell membrane. Besides being responsible for movement, they are also important in assisting protozoa to capture solid food. Sanitary engineers usually consider *Ciliata* to be divided into two types: free-swimming and stalked. The free-swimming type must swim after bacteria. They require a great deal of food, because they expend so much energy in swimming. *Paramecium* is a free-swimming ciliate that is important in effluent treatment. Stalked ciliates may be attached to something solid and must catch food as it passes. Because their movement is limited or free-floating, they require less food for energy. *Vorticella* is a stalked ciliate that is important in biological treatment processes, especially in the activated sludge process.

Rotifers

The rotifer is an aerobic, heterotrophic, multicellular organism. Its name is derived from the fact that it has two sets of rotating cilia on its head, which are used for motility and capturing food. Rotifers are very effective in consuming dispersed and flocculated bacteria and small particles of organic matter. Their presence in mixed liquor indicates a highly efficient aerobic biological purification process.

Worms

Worms are characteristic higher life forms that appear in activated sludge systems with very high sludge age.

Bacterial Growth

Bacteria generally reproduce by binary fission. The time required for each fission, which is termed the generation time, can vary from days to less than 20 minutes. The general growth pattern of bacteria in a batch culture is shown in Fig. 23.1. Initially, a small number of organisms are inoculated into a culture medium, and the number of viable

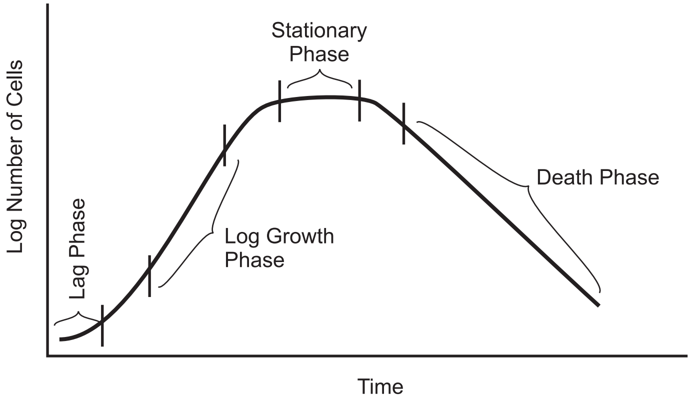

FIGURE 23.1 Typical bacteria growth curve.

organisms is recorded as a function of time. The growth pattern based on the number of cells has four more or less distinct phases:

1. Lag Phase—Upon addition of an inoculum to a culture medium, the lag phase represents the time required for organisms to acclimate to their new environment.
2. Log Growth Phase—During this period, cells divide at a rate determined by their generation time and their ability to process food (constant percentage growth rate).
3. Stationary Phase—Here, the population remains stationary. Stationary growth occurs because cells have exhausted substrate or nutrients necessary for growth, and growth of new cells is offset by death of old cells.
4. Log Death Phase—During this phase, the bacterial death rate exceeds production of new cells. The death rate is usually a function of the viable population and environmental characteristics. In some cases, the log death phase is the inverse of the log growth phase.

The growth pattern is described in terms of the variation of the mass of microorganisms with time. This growth pattern consists of the following four phases:

1. Log Growth Phase—There is always an excess amount of food surrounding the microorganisms, and the rate of metabolism and growth is related to the ability of the microorganism to consume food.
2. Stationary Phase—The availability of food and the microorganisms are in balance.

3. Declining Growth Phase—The rate of growth and hence the mass of bacteria decrease because of limitations in the food supply.
4. Endogenous Phase—Microorganisms are forced to metabolize their own protoplasm without replacement because the concentration of available food is at a minimum. During this phase, a phenomenon known as lysis can occur, in which nutrients remaining in dead cells diffuse out to furnish remaining live cells with food.

It is important to note that the preceding discussions concerned a single population of microorganisms. Biological treatment units are composed of complex, interrelated, mixed biological populations, with each particular microorganism in the system having its own growth curve. The position and shape of a particular growth curve in the system, on a time scale, depends on food and nutrients available and environmental factors such as temperature, pH, and whether the system is aerobic or anaerobic.

Bacterial Oxidation

As previously discussed, secondary treatment or the conversion of organic matter to stable end products is accomplished aerobically, anaerobically, or facultatively (alternating presence and absence of oxygen), using suspended growth or attached growth systems. A portion of organic material is oxidized to obtain energy necessary for synthesis of new cell mass. As organics are removed, microorganism cell matter is metabolized to stable end products. In most biological treatment systems, these processes occur simultaneously.

The three processes may be represented as follows for an aerobic process:

1. Oxidation:

$$\begin{gathered}\text{Organic matter (COHNS)} + O_2 + \text{bacteria} \rightarrow \\ CO_2 + H_2O + \text{other energy end products}\end{gathered} \tag{23.3}$$

2. Synthesis:

$$\begin{gathered}\text{Organic matter (COHNS)} + O_2 + \text{bacteria} + \text{energy} \rightarrow \\ C_5H_7NO_2 \text{ (new bacterial cells)}\end{gathered} \tag{23.4}$$

3. Endogenous respiration:

$$C_5H_7NO_2 + 5O_2 \rightarrow 5CO_2 + NH_3 + 2H_2O + \text{energy} \tag{23.5}$$

In these equations, COHNS represents organic matter in effluent. The formula $C_5H_7NO_2$, which represents bacteria cells, is a generalized value obtained from experimental studies. Although the endogenous respiration reaction is shown as resulting in relatively simple end products and energy, stable organic end products are also formed.

Biological Treatment Control Parameters

To ensure a favorable environment to promote the reactions involved in the biological treatment process, the following parameters must be controlled:

- pH and alkalinity
- Temperature
- Oxygen requirements
- Nutrient requirements
- Solids separation
- Biological solids recirculation
- Aeration capacity
- Mixing energy
- Hydraulic retention time
- Solids retention time

Biological waste treatment removes organic matter in effluent in much the same manner as naturally occurring stream biota would in surface receiving waters. However, there is usually not as much time to break down solid organic matter in biological treatment. Generally, microorganisms in biological waste treatment work most efficiently on dissolved organic matter. These active microorganisms are a relatively small fraction of the total biological process biomass. Certain constituents adversely affect the biological treatment process. Major constituents and their effects on the biological treatment process are shown in Table 23.3.

Certain substances present in municipal and industrial effluents are more biodegradable than others. A relative comparison of biodegradability of various constituents commonly found in effluent is shown in Table 23.4.

pH and Alkalinity

pH of effluent is not always a problem. However, in biological treatment, pH can drop mainly because of nitrate and carbon dioxide generation from BOD and nitrogen. Operation of most biological processes is limited to a pH range of 5 to 9 (optimum is 6.5–7.5). If effluent does not contain enough alkalinity (bicarbonate), biological production of carbon dioxide and nitrate can drop pH out of the optimum range. If pH drops below the optimum range, caustics, limes, or other alkalis can be added as needed.

Constituent	Condition*
Ammonia nitrogen	Needed for growth; too low a level can inhibit growth; high levels of unionized ammonia can inhibit nitrification.
Phosphate	Needed for growth; too low a level can inhibit growth.
Calcium and magnesium	Very small amounts needed for growth.
Chloride	Corrosive; toxic to microorganisms at very high levels.
Mercury	Toxic to microorganisms at designated levels.
Other heavy metals	Toxic to microorganisms at designated levels.
Sulfate	Needed in small amounts.
Sulfide	Corrosive; depletes oxygen; toxic for nitrification bacteria.
Petrochemicals	Toxic to microorganisms at high levels.
Phenol compounds	Toxic to microorganisms at high levels until organisms acclimate.
Surfactants	Cause foaming and can decrease oxygen transfer efficiency.

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*Toxicity levels are dependent upon average and peak loadings.

Table 23.3 Biological Treatment System’s Critical Constituents

Easily Biodegradable	Slower or Moderately Biodegradable			Less Easily Biodegradable
Sugars Alcohols	Ketones Phenol compounds	Organic acids	Esters Ethers	Cellulose Fats Lignins Polymeric compounds Hydrocarbons: Aliphatic Aromatic Alkyl, aryl Chlorinated aromatics

Table 23.4 Relative Biodegradability of Organic Compounds

Alkalinity is the measured capacity of a solution's ability to react with acid [usually sulfuric acid (H_2SO_4)] to a predetermined pH such as 4.2. The higher the alkalinity, the higher the demands for the neutralizing agent (or acid) for a pH drop. Therefore, pH does not drop much even with carbon dioxide and nitrate formation when effluent alkalinity is high.

Systems designed for nitrification and denitrification require pH between 7.2 and 8.0. At pH above or below this level, nitrification may slow down. At pH < 6, nitrification completely stops.

Temperature

Temperature affects all biological processes. Biological oxidation rates increase to a maximum at about 95°F (35°C) for most treatment systems. At temperatures greater than 95°F (35°C), treatment efficiency decreases by reducing bacterial floc formation. Temperatures in excess of 99°F (37°C) show a definite effect on biological systems. It is possible, however, in certain wastes, to operate efficiently at somewhat higher temperatures. Lower temperatures than 50°F (10°C) also affect performance of biological processes, especially nitrification efficiency.

The rate of biological activity is influenced by temperature because of the depth of penetration of oxygen into the floc or film. Oxygen penetration increases as temperature decreases, since oxygen is not used as quickly at floc surfaces and greater numbers of organisms per unit surface can react. Oxygen solubility also increases as temperature decreases.

Sludge Production

Sludge production in a biological treatment system is expressed as the net effect of the following two processes:

1. Synthesis of new organisms resulting from assimilation of organic matter removed
2. Reduction of the mass of organisms under aeration by the process of die off and oxidation over an extended period (known as endogenous respiration)

Figure 23.2 shows the pathway of carbon contained in effluent.

As a result, net sludge production is mainly functions of total BOD treated in the process and solids retention time (SRT), which is also known as mean cell residence time (MCRT). For the activated sludge process where SRT is 5 to 10 days, sludge yield is typically 0.5 to 0.6 lb as dry mass when 1 lb of domestic BOD (0.5–0.6 kg/kg) is treated, and lower with longer SRT. Sludge yield is different for different types of industrial effluents.

Oxygen Requirements

Theoretical oxygen requirements can be determined from the five-day BOD (BOD_5) of effluent, less the amount of organisms wasted from

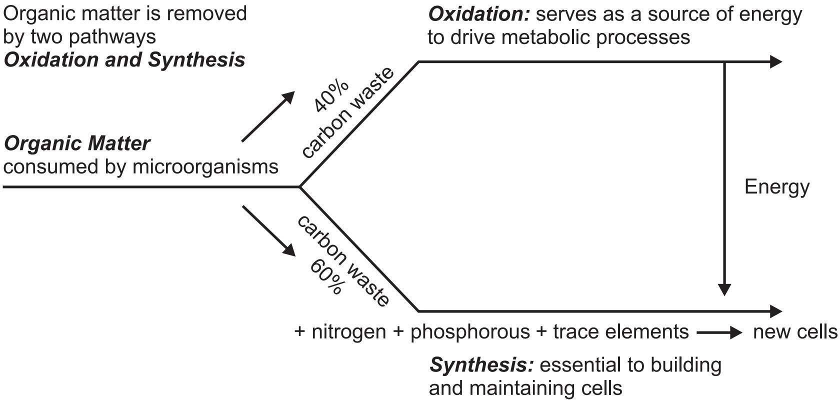

FIGURE 23.2 Carbon pathways in effluent.

the system per day. If all of the BOD_5 were converted to end products (CO_2 and H_2O), total oxygen demand would be computed by converting the BOD_5 to BOD_L (all carbonaceous BOD converted to end products), using an appropriate conversion factor. A portion of the waste is converted to cell structure, and is removed from the system, however. Therefore, if BOD_L of the wasted cells is subtracted from the total, the remaining amount represents the amount of oxygen that must be supplied to the system. It is known that one mole of cells is equal to 1.42 times the concentration of cells [Eq. (23.6)]. The theoretical oxygen requirements for removal of carbonaceous organic matter in effluent by an activated sludge system are:

$$OD_C = [Q(S' - S)f_C/f_{BOD}] - 1.42P_x \tag{23.6}$$

where OD_C = carbonaceous oxygen demand, lb O_2/d (kg O_2/d)
Q = influent effluent flow rate, mgd (m^3/d)
S' = influent BOD, mg/L
S = effluent BOD, mg/L
f_C = unit conversion factor, 8.34 lb/gal for US units [(1000 L/m^3)(1 kg/10^6 mg) = 1/1000 for metric units]
f_{BOD} = conversion factor for converting BOD_5 to BOD_L, dimensionless (0.68 for municipal effluent)
P_x = net sludge production in terms of volatile solids, lb/d (kg/d)

When nitrification occurs, the total oxygen requirement is that required for removal of carbonaceous organic matter [Eq. (23.6)], plus oxygen required for conversion of ammonia to nitrate as follows:

$$OD_N = 4.57Q(N_0 - N)f_C \tag{23.7}$$

where OD_N = nitrification oxygen demand, lb O_2/d (kg O_2/d)
Q = influent effluent flow rate, mgd (m^3/d)
N_0 = influent total Kjeldahl nitrogen (TKN), mg/L
N = effluent total Kjeldahl nitrogen (TKN), mg/L
4.57 = conversion factor for amount of oxygen needed for complete oxidation of TKN
f_C = unit conversion factor, 8.34 lb/gal for US units [(1000 L/m^3) (1 kg/10^6 mg) = 1/1000 for metric units]

Based on the oxygen requirement, the aeration rate is calculated considering oxygen transfer efficiency, and the oxygen content in air using the Eq. (23.8). Oxygen transfer efficiency depends on mixed liquor suspended solids (MLSS) in the aeration basin, diffuser type, temperature, basin depth, residual DO, etc. In an aeration basin having a depth of 15 ft (4.6 m), overall oxygen transfer efficiency is typically 8 to 12% with coarse bubble air diffusers. Fine bubble diffuser efficiency is in the range of 20 to 30%. Many plants have converted from coarse to fine bubbles to save energy.

$$\mathrm{AR} = \mathrm{O}/[4(\varepsilon)(d)] \tag{23.8}$$

where AR = aeration rate, m^3 air/min (1 m^3 = 35.3 ft^3)
O = oxygen requirement, kg O_2/d
ε = specific oxygen transfer efficiency, /m (commonly 0.015–0.03/m)
d = aeration basin depth, m

A very rough rule-of-thumb for the total amount of oxygen that should be supplied to a biological effluent treatment plant is approximately 2 to 4 lb O_2/lb BOD removed (2–4 kg/kg) for low loaded systems [0.05 lb BOD/lb MLSS (0.05 kg/kg)], and 1.5 to 2.5 lb O_2/lb BOD removed (1.5–2.5 kg/kg) for medium loaded systems [0.1–0.2 lb BOD/lb MLSS (0.1–0.2 kg/kg)].

Nutrient Requirements

In general, a ratio of BOD/nitrogen/phosphorus of 100/5/1 is recommended for maintaining the best biological conditions. For healthy growth, it is important to have sufficient nutrients by maintaining a small excess in the final effluent. Approximately 1 or 2 mg/L nitrogen [as ammonia (NH_3)] and soluble orthophosphate (filtered sample) in the effluent is sufficient. Phosphoric acid and mono, di, and trisodium phosphate are used as sources of phosphorous. Polyphosphates and hexametaphosphate are not a readily available source of phosphate for microorganisms, and should not be used. Anhydrous or aqueous ammonia and urea are used as sources of nitrogen. Ammonium phosphate can also be used, but it is difficult to meet the different demands for nitrogen and phosphorus additions.

Element	Bacterial Composition, mg/g biomass COD*	Minimum Influent Concentration, mg/L
N	87	10
P	17	2
K	10	1.2
Ca	10	1.2
Mg	7	0.8
S	6	0.7
Na	3	0.4
Cl	3	0.4
Fe	2	0.2
Zn	0.2	0.02
Mn	0.1	0.01

*Chemical oxygen demand.

Table 23.5 Typical Substrate and Nutrient Requirements for Effluent with 200 mg/L BOD (300 mg/L COD)

In addition to nitrogen and phosphorous, many other mineral elements are essential for proper metabolic activity of microorganisms involved in waste treatment. Table 23.5 summarizes minimum nutrient requirements for effluent having a BOD of 200 mg/L. At higher BOD, minimum requirements of the nutrients increase proportionally.

Municipal effluents usually contain enough of all micronutrients. However, many industrial effluents suffer from nutrient deficiency due to a narrow range of raw materials. For example, effluents in the chemical and pharmaceutical industries often contain low levels of mineral elements, while organic contents represented by BOD and chemical oxygen demand (COD) are very high. For proper biological treatment, micronutrients such as K, Ca, Mg, S, and Fe should be added as needed along with N and P.

Solids Separation

One of the most important aspects of biological waste treatment is in the design of facilities used to separate biological solids from treated effluent. Secondary sedimentation must perform two functions:

1. Separate MLSS from treated effluent
2. Thicken return sludge and waste activated sludge

Both functions are affected by surface area and depth of the sedimentation basin. Ample volume must be provided for storage of solids during periods in which sustained peak plant loadings are experienced. In addition, peak daily flow rate variations must be considered because they affect sludge removal requirements. The secondary clarifier/thickener must be sized for either the hydraulic loading (gpd/ft^2 or m^3/[h·m^2]), or solids flux (lb solids/[d·ft^2] or kg/[h·m^2]). In most cases, solids flux or loading is the critical parameter.

Return Sludge Requirements

The purpose of the return of settled solids is to maintain a sufficient concentration of activated sludge in the aeration tank, so that the required degree of treatment can be obtained in the time interval desired. Return of activated sludge from the clarifier to the inlet of the aeration tank is essential to the process.

Solids tend to form a sludge blanket in the bottom of the clarifier/thicker, which varies in thickness from time to time. If solids thickening capacity of the secondary clarifier is inadequate, solids may fill the entire depth of the tank at peak flows. Return sludge pump capacities vary between 25 and over 200% of influent flow, depending upon operational strategy and condition.

Activated Sludge Process

The activated sludge process was developed in England in 1914, and was so named because it involves production of an active mass of microorganisms capable of stabilizing organic content of waste in the presence of DO. Activated sludge is probably the most versatile of biological treatment processes. The process has found wide application in both domestic and industrial effluent treatment.

Activated sludge is a biological contact process where bacteria, protozoa, and small organisms such as rotifers are commonly found. Bacteria are the most important group of microorganisms, because they are responsible for the structural and functional activity of the activated sludge floc. All types of bacteria (except pathogens) make up activated sludge. The predominant type is determined by the nature of organic substances in effluent, mode of operation of the plant, and environmental conditions present for organisms in the process.

The conventional activated sludge process consists of an aeration tank, secondary clarifier, method of returning sludge to the aeration tank, and means of wasting excess sludge from the system (see Fig. 23.3). Sludge wasting is accomplished from the recycle or mixed liquor line. The flow model is plug flow with clarifier underflow recycle. Both influent settled effluent, and recycled sludge enter the tank at the head end, and are aerated for a period of 4 to 12 hours. Influent effluent and recycled sludge are mixed by the action of diffused or mechanical aeration, which is constant in a well-operated system as mixed liquor moves down the tank.

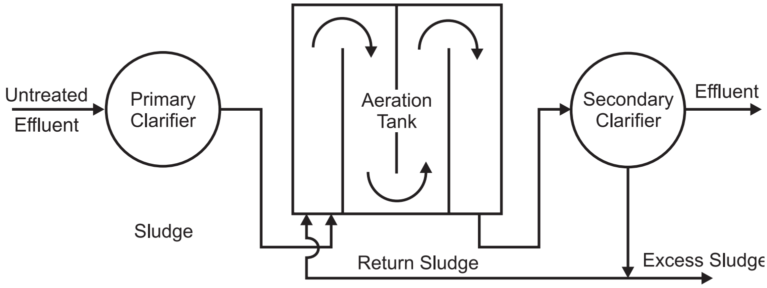

Figure 23.3 Conventional plug flow activated sludge process.

During this period, absorption, flocculation, and oxidation of organic matter occur. Mixed liquor is settled in the activated sludge clarifier/thickener, and sludge is returned at a rate of approximately 25 to 100% of the influent flow rate.

Activated Sludge Process Equipment

All activated sludge processes have certain process equipment similarities. These are discussed in the following paragraphs.

Aeration Tanks

Aeration tanks used in activated sludge processes are usually constructed of reinforced concrete and left open to the atmosphere. A cross section of a typical aeration tank is shown in Fig. 23.4.

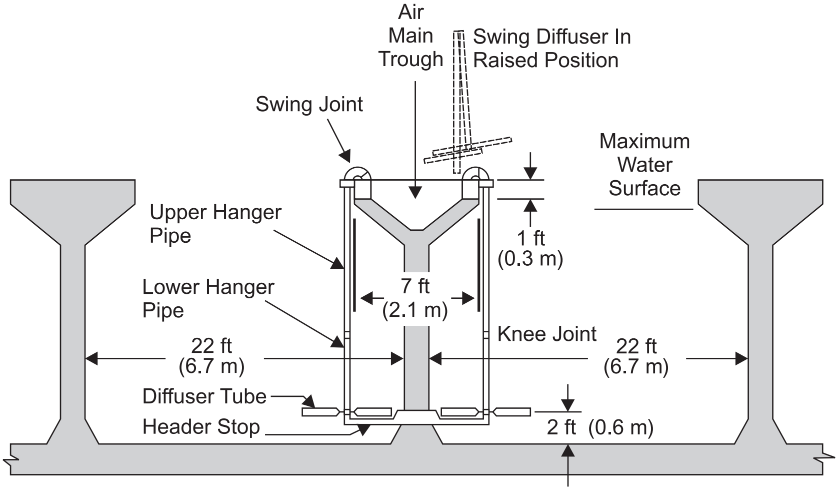

Figure 23.4 Cross section of typical activated sludge aeration tank.

The rectangular shape permits common-wall construction for multiple tanks. If total capacity exceeds 5000 ft^3 (142 m^3), the total aeration tank volume required should be divided among two or more units capable of independent operation. Total capacity required is determined from the biological process design.

If effluent is to be aerated with diffused air, geometry of the tank may significantly affect aeration efficiency and amount of mixing obtained. Depth of effluent in the tank should be between 10 and 16 ft (3–4.9 m), so that diffusers can work efficiently. Freeboard should be 1 to 2 ft (0.3–0.61 m) above the waterline. Width of the tank in relation to its depth is important, if spiral-flow mixing is used. The width-to-depth ratio for such tanks may vary from 1.0:1 to 2.2:1. This limits the width of a tank channel to 20 to 36 ft (6.1–11 m).

In large plants, channels become quite long, sometimes longer than 500 ft (152 m) per tank, and tanks may consist of one to four channels with round-the-end flow in multiple-channel tanks.

Large plants should contain not less than four tanks, and preferably six to eight or more. Some of the largest plants contain 30 to 40 tanks arranged in several groups or batteries.

Figure 23.4 is based on the use of coarse bubble air diffusers for transfer of oxygen to the liquid. Today, the use of fine bubble diffusers installed across the width and length of the aeration basin are preferred, to reduce energy use. In fact, many plants originally built with coarse bubble diffusers have been modified to fine bubble diffusers to reduce energy costs.

Secondary Clarifier

A secondary clarifier is constructed and operated very much like a primary clarifier, except that the secondary tank follows the biological treatment process (i.e., trickling filter or activated sludge). The function of secondary clarifiers varies with the method of biological treatment used. Clarifiers following trickling filters are used to separate biological solids that have broken away from the filter media. Clarifiers in an activated sludge system, however, serve two purposes. Besides providing a clarified effluent, they provide a concentrated source of return sludge to the aeration basin for process control.

Like primary clarifiers, secondary tanks may be round or rectangular. These tanks may be designed for natural settling or chemically aided settling, with tank size being related to one of the following:

- Surface loading rates in gallons per square foot (m^3/m^2) of floor area per day
- Solids loading rate in pounds (kilograms) of solids per square foot (m^2) of floor area per day
- Flow-through velocity in feet per minute (m/min) (rectangular tanks)

- Weir placement and loading rates in gallons (m^3) per day per linear foot (meter) weir length
- Retention time of settled sludge in hours

Clarifiers in activated sludge systems must be designed not only for hydraulic overflow rates, but also for solids loading rates (solids flux). This is because both clarification and thickening are needed in activated sludge clarifiers. At higher MLSS values (i.e., more than about 1500 mg/L), ability of the clarifier to thicken solids becomes the controlling factor. Solids loading rate becomes critical in determining tank size and operation limitations. As a result, design of clarifiers following the activated sludge process is usually based on average and peak overflow rates and solids loadings.

Performance of secondary effluent treatment systems is determined by comparing the quality of overflow from secondary clarifiers to that of incoming effluent. The biological treatment unit converts some of the soluble and insoluble organics to suspended organic solids. However, the treatment process is successful only if these organic solids are removed in the secondary clarifiers/thickeners. Secondary clarifier operational variables have the most critical effect on overall plant performance. Table 23.6 provides typical operational loading parameters of secondary clarifiers for treatment of various industrial effluents by biological treatment.

Aeration Equipment

The three basic methods of aerating effluent are:

1. Introduce air or oxygen into effluent with submerged porous diffusers.
2. Agitate effluent mechanically to promote solution of oxygen from the atmosphere above the liquid being aerated (mechanical aerator).
3. Use aspirators (eductors) with or without blowers (jet aeration).

	Solids Flux		Overflow Rate	
Industry	**lb/(d·ft²)**	**kg/(d·m²)**	**gpd/ft²**	**m³/(d·m²)**
Pulp and paper	18–25	88–122	400–800	16–33
Petrochemical	10–15	49–73	300–600	12–24
Refinery biological contactor	8–12	39–59	300–600	12–24
Secondary	20–29	98–142	400–800	16–33
Nitrified effluent	17–24	83–117	400–600	16–24

TABLE 23.6 Typical Biological Secondary Settling Tank Operational Loading Parameters

Bubble Size	Transfer Efficiency	Description
Fine	High	Ceramically bonded grains of fused crystalline aluminum oxide. Vitreous silicate bonded grains of pure silica. Resin bonded grains of pure silica.
Medium	Medium	Plastic wrapped diffuser tubes Woven fabric sock or sleeve diffusers
Coarse	Low	Various orifice devices Sparger air escapes from periphery of flexible or rigid disc that is displaced when manifold pressure exceeds the head on the disc. Slot orifice injectors

Table 23.7 Description of Diffuse Air Aeration Devices

The amount of air used per pound (kilogram) of BOD removed varies greatly from one plant to another and for different industries. Comparing air use at different plants is risky because of different loading rates, control criteria, biological treatment rates, and operating procedures.

Diffused Aeration A diffused air system consists of diffusers that are submerged in effluent, header pipes, air mains, and blowers and appurtenances through which air is supplied.

The diffusers most commonly used in aeration systems are designed to produce fine, medium, or coarse (relatively large) bubbles (see Table 23.7). Fine bubble diffusers constructed of neoprene and other materials are most commonly used today due to their high oxygen transfer efficiency (lower power consumption).

Mechanical Aerators The most commonly used types of mechanical aerators are surface and submerged turbine aerators. With surface aerators, oxygen is entrained both from the atmosphere and from air or pure oxygen introduced in the tank bottom. In either case, the pumping action of the aerator, and that of the turbine, help to keep the contents of the aeration tank mixed. Both types are described here, along with aerator performance and energy required for mixing.

Surface Aerators—Mechanical surface aerators are the simplest type of aerators (see Figs. 23.5–23.7). They are available in sizes from 1 to 100 hp (0.75–75 kW). They consist of submerged or partially submerged impellers that are attached to motors, which are mounted on

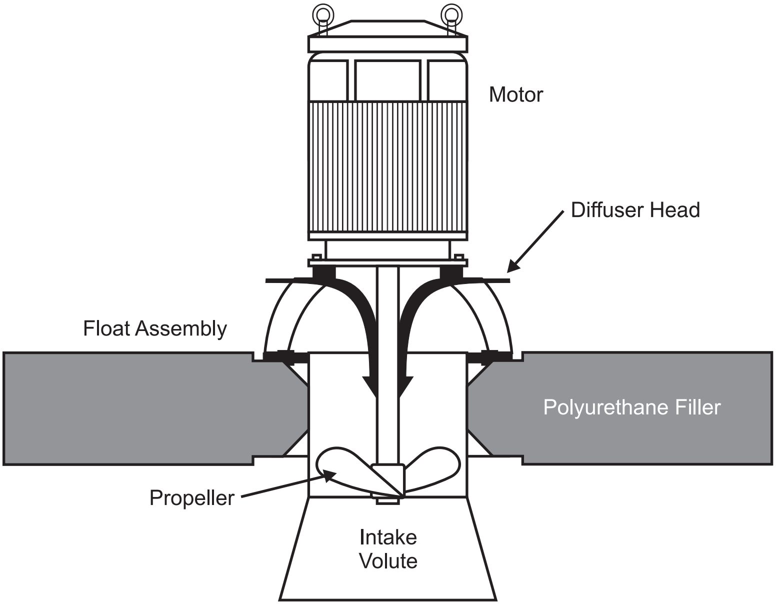

Figure 23.5 Surface mechanical aerator.

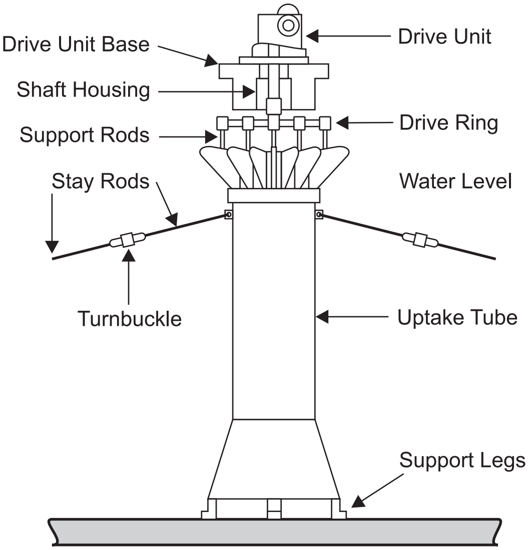

Figure 23.6 Simplex cone mechanical aerator.

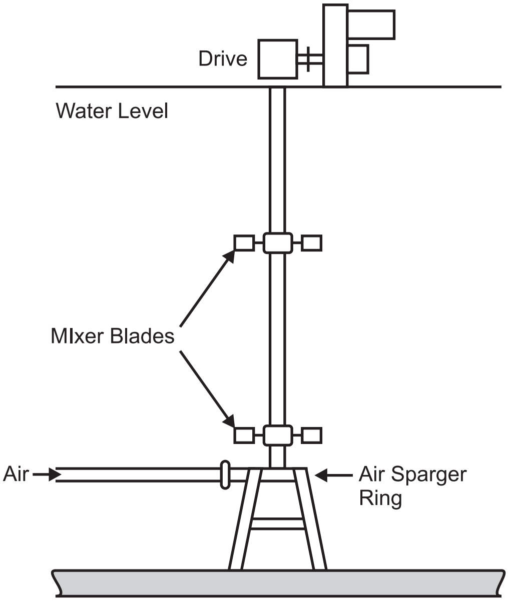

FIGURE 23.7 Turbine mechanical aerator.

floats or fixed structures. Impellers are fabricated from steel, cast iron, noncorrosive alloys, and fiberglass-reinforced plastic, which are used to agitate effluent vigorously, entraining air in the effluent and causing a rapid change in the air-water interface to facilitate solution of oxygen. Surface aerators may be classified as low or high spec, according to the speed of rotation of the impeller. In low-speed aerators, the impeller is driven through a reduction gear by an electric motor. Motor and gearbox are usually mounted on a platform that is supported either by piers extending to the bottom of the tank, or by beams that span the tank. They have also been mounted on floats. The propeller for high-speed aerators is driven at the electrical motor speed. The high speed of the propeller and the smaller diameter (as compared to low-speed units) results in lower oxygen transfer efficiency.

Submerged Turbine Aerators—Most mechanical surface aerators are upflow types that rely on violent agitation of the surface, and air entrainment for oxygen transfer efficiency. However, with turbine aerators, air or pure oxygen may also be introduced by diffusion into the effluent beneath the impeller of downflow or radial aerators. (Not commonly used due to low transfer efficiency.) The impeller is used to disperse air bubbles and mix the tank contents. A draft tube may be used with either upflow or low-speed models in deep aeration tanks. The draft tube is a cylinder with flared ends mounted concentrically, with the impeller extending from just above the floor of the aeration tank to just beneath the impeller.

Mechanical Aerator Performance—Surface aerators are rated in terms of their oxygen transfer rate expressed as pounds (kilograms) of oxygen per horsepower-hour (kilowatt-hour) at standard conditions, which exist when the temperature is 68°F (20°C), initial DO is 0.0 mg/L, and test liquid is tap water. Commercial-size surface aerators now available range in efficiency from 2 to 3.5 lb $O_2/[\mathrm{hp \cdot h}]$ (1.2–2.1 kg/kWh) at standard conditions. The lower value is for motor speed aerators, while the higher is for low-speed units.

Energy Requirement for Mixing—As with diffused air systems, size and shape of the aeration tank are very important, if good mixing is to be achieved. Aeration tanks may be square or rectangular and may contain one or more units. Water depth may vary from 4 to 12 ft (1.2–3.7 m) when using surface aerators. Depths up to 35 ft (10.7 m) have been used with draft-tube mixers.

In diffused air systems, the air requirement to ensure good mixing varies from 20 to 30 $\mathrm{ft^3/1000\ ft^3}$ (20–30 $\mathrm{m^3/1000\ m^3}$) of tank volume.

Typical power requirements for maintaining a completely mixed flow regime with mechanical aerators vary from 0.6 to 1.15 $\mathrm{hp/1000\ ft^3}$ (16–30 $\mathrm{kW/1000\ m^3}$), depending on design of the aerator and geometry of the tank, lagoon, or basin. In the design of aerated lagoons for treatment of domestic wastes, it is extremely important that the mixing power requirement be checked, because in most instances it is the controlling factor. With both the diffused air systems and mechanical aerators, power required for oxygen transfer is usually less than that required for mixing to keep solids in suspension.

Jet Aeration Jet aeration consists of an eductor (aspirator) pump and blower. Pump suction is from the aeration basin and discharges to the inlet of the eductor. The blower supplies air to the venturi throat of the eductor. Water velocity through and size of the venturi throat creates small air bubbles for efficient oxygen transfer to liquid in the aeration basin. It has been found in some cases that pumping biological flocs through the eductor breaks up the floc, resulting in solids carryover from secondary clarifiers.

Table 23.8 shows typical performance characteristics for air diffusers used in effluent treatment.

Oxygen Equipment

There are two pure oxygen generator designs: the traditional cryogenic air separation process for large applications and a pressure swing adsorption (PSA) system for the somewhat smaller and more common plant sizes.

Type of Aerator	Water Depth, ft (m)	Oxygen Transfer Efficiency, %	Aerator Rating	
			lb O_2/(hp·h)	kg O_2/kWh
Fine bubble:				
Tubes-spiral roll	15 (4.6)	15–20	6–8	3.6–4.9
Domes-full floor coverage	15 (4.6)	25–35	11–12.5	6.7–7.6
Coarse bubble:				
Tubes	15 (4.6)	10–13	4–5	2.4–3
Spargers	14.5 (4.4)	6–8	2–3.5	1.2–2.1
Jet aerators	15 (4.6)	15–24	4–5	2.4–3
Static aerators	15 (4.6)	10–11	4–4.5	2.4–2.7
Surface aerators:				
Low speed	12 (3.7)	–	3–3.5	1.8–2.1
High speed	8 (2.4)	–	2–2.5	1.2–1.5

Table 23.8 Air Diffuser Performance Characteristics

The cryogenic air separation process involves liquefaction of air, followed by fractional distillation to separate it into its components (mainly nitrogen and oxygen).

The PSA system uses a multibed adsorption process to provide a continuous flow of oxygen gas. Feed air is compressed and passed through one of the adsorbers. The adsorbent removes carbon dioxide, water, and nitrogen gas, and produces relatively high-purity oxygen. While one bed is adsorbing, the others are in various stages of regeneration.

The concept of the PSA generator is that oxygen is separated from feed air by adsorption at high pressure, and the adsorbent is regenerated by "blowdown" to low pressure. The process operates on a repeated cycle having two basic steps: adsorption and regeneration.

Activated Sludge Process Control Concepts

Common control methods used for the activated sludge process include:

- Solids retention time (SRT)
- Food-to-microorganism ratio (F/M)
- Constant MLSS
- Return activated sludge control

Objectives of activated sludge secondary treatment are to biologically oxidize waste organic content aerobically and to remove excess new cell growth solids before discharge to receiving waters. Each treatment plant operates within a range of process control parameters based on original plant design that tends to keep the biological process in a steady state condition, as long as raw waste influent characteristics do not change too abruptly. By maintaining process parameters within a narrow range, swings in process efficiency that may result from shock loads or upsets are minimized, and continuously high organic removal efficiency is assured.

Solids Retention Time

Solids retention time (SRT), also called MCRT or sludge age, is calculated by dividing the total quantity of sludge in the aeration basin and clarifier by daily sludge losses through waste activated sludge and effluent. Equation (23.9) shows the calculation:

$$\mathrm{SRT} = \frac{X_1 V_1 + X_2 V_2}{X_X Q_X + X_e Q_e} \tag{23.9}$$

where SRT = solids retention time, days
X_1 = MLSS in aeration basin, mg/L
X_2 = MLSS in clarifier, mg/L
X_x = MLSS in waste activated sludge, mg/L
X_e = MLSS in effluent, mg/L
V_1 = volume of aeration basin, gal (m^3)
V_2 = volume of clarifier, gal (m^3)
Q_x = effluent flow rate, gpd (m^3/d)
Q_e = waste activated sludge flow rate, gpd (m^3/d)

The activated sludge system can be controlled based on keeping the SRT value at a constant level. (See Table 23.9 for recommended ranges for activated sludge processes.)

If SRT overly exceeds the recommended range, which directly means scarce food condition or low F/M ratio, sludge floc can be dismantled, and pin floc can be formed. This condition is often accompanied by solids loss and an increase in effluent turbidity from the secondary clarifier.

When the system is operated at lower than recommended SRT, a condition commonly called "young sludge" may result. This light, fluffy, buoyant sludge, also called straggler floc, settles slowly. This is witnessed in a clarifier when these fluffy floc particles are pulled over weirs even though the effluent may be relatively clear. This condition may appear in the aeration basin as white billowy foam. These conditions are typical of activated sludge systems just after startup. In addition, SRT lower than five days is not sufficient to grow enough slowly growing autotrophic microorganisms that oxidize nitrogen. Consequently, nitrification is not possible at low SRT.

Process Description	Flow Regime	SRT, days	F/M*	Aerator Loading[†]	MLSS, mg/L	Detention Time, h	Recirculation Ratio
Conventional	Plug flow	5–15	0.2–0.4 (0.1–0.2)	20–40 (320–640)	1500–3000	4–8	0.25–0.5
Complete mix	Complete mix	5–15	0.2–0.6 (0.1–0.3)	50–120 (800–1920)	3000–6000	3–5	0.25–1.0
Step aeration	Plug flow	5–15	0.2–0.4 (0.1–0.2)	40–60 (640–960)	2000–3500	3–5	0.25–0.75
Contact stabilization	Plug flow	5–15	0.2–0.6 (0.1–0.3)	30–75 (480–1200)	1000–4000[§] 4000–10 000	0.5–1.5[§]	0.5–1.5
Extended aeration	Complete mix	20–30	0.05–0.15 (0.02–0.07)	10–15 (160–240)	2000–6000	24	0.5–2.0
Pure oxygen systems	Complete mix, reactors in series	8–20	0.25–1.0 (0.1–0.5)	100–250 (1600–4000)	4000–8000	2–5	0.25–0.5
Aerated lagoon	Complete mix	5–120	‡	‡	2000–6000	120–1000	0

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*lb BOD$_5$ MLVSS/d (kg/d).

[†] lb BOD$_5$/1000 ft^3 (kg/1000 m^3) tank volume.

[‡] Depends on waste loading.

[§] Contact unit.

[¶] Stabilization tank.

Table 23.9 Summary of Operating Data for Activated Sludge Processes

The main variable in SRT control is sludge wasting rate. Generally, operation involves finding an SRT level at which the plant achieves optimum effluent quality. When the SRT value has been reduced to proper levels and conditions in the treatment system improved, then operator stops or decreases the sludge-wasting rate to maintain constant SRT. There are conditions and periods depending on loading rates, changes in flow rates, and presence of toxic shocks, where SRT levels should be increased or decreased.

Food-to-Microorganism Ratio

A term for expressing organic loading of an activated sludge process is F/M ratio, and is a critical factor in process design and operation, especially in determining aeration basin volume. F/M is usually defined as:

$$\mathrm{F/M} = \frac{Q_0(S_0 - S_e)}{X_A V_A} \tag{23.10}$$

where F/M = food-to-microorganism ratio, lb BOD/(lb MLVSS · d) [kg BOD/(kg MLVSS · d)]
Q_0 = influent flow rate, gpd (m^3/d)
S_0 = influent BOD_5, mg/L
S_e = effluent BOD_5, mg/L
X_A = mixed liquor volatile suspended solids (MLVSS) in aeration basin, mg/L
V_A = aeration basin volume, gal (m^3)

If only COD is available for domestic effluent, divide the COD by 1.5 to obtain approximate BOD_5. Similarly, MLSS can be multiplied by 0.75 to obtain an approximate MLVSS. BOD/COD and MLSS/MLVSS ratios for industrial effluent can vary significantly depending on the type of industrial process.

F/M and MLVSS are important design criteria for sizing the aeration basin and along with sludge age are important operating criteria.

Mixed Liquor Suspended Solids and Mixed Liquor Volatile Suspended Solids

Suspended solids level is one of the most important control parameters in biological effluent treatment processes. It is not only directly related with sludge settling properties and effluent quality, but also related with F/M ratio that is in turn related with all aspects of sludge properties.

In general, MLSS represent TSS, irrespective of biological activity. Measurement is expressed as an empirical test result that reports the quantity of suspended solids carried in the aeration basin. Usually, glass filters having a pore size of 1.2 μm are used.

On the other hand, MLVSS represent the organic portion of MLSS, which is used to represent biomass. This is also expressed as an empirical test result (the amount of solids that was lost in volatilization at 550°C); this test reports roughly the portion of MLSS that has the active microbial population used to absorb and degrade soluble organic matter in wastes.

The activated sludge system can be controlled based on a constant MLSS level much the same way as the SRT control approach. (See Table 23.9 for recommended ranges for activated sludge processes.) Similar conditions occur in the process due to MLSS concentrations higher and lower carried in the activated sludge system (as described for respective conditions for SRT levels). As with SRT control, the main variable for maintaining constant MLSS is the sludge-wasting rate. After an acceptable MLSS level is determined for operation of the system, the sludge-wasting rate is controlled to maintain this level. When the MLSS level increases above the determined optimum range, then the plant operator starts or increases the sludge-wasting rate. When the MLSS level decreases below the range, then the operator stops or decreases the sludge-wasting rate, to maintain a constant MLSS level in the system and F/M in the optimum range.

Sludge Blanket Depth

Sludge blanket depth in the clarifier should be measured at the same time each day and at the same point on the clarifier bridge. The best time is during the period of maximum daily flow, because the clarifier is operating under the highest solids loading rate. Adjustments in the recycle activated sludge (RAS) flow rate should be needed only occasionally if the activated sludge process is operating properly.

An additional advantage of monitoring sludge blanket depth is that problems, such as improperly operating sludge collection equipment, can be observed due to irregularities in blanket depth. A plugged pick-up on a clarifier sludge collection system would cause sludge depth to increase in the area of the pick-up, and decrease in areas where properly operating pick-ups are located. These irregularities in sludge blanket depth are easily monitored by measuring profiles of blanket depth across the clarifier.

Other Parameters Used to Evaluate Performance

Other parameters can be used to track performance of the activated sludge process. These parameters are also effective in assessing health of microorganisms and can be used to determine where problems exist. Some common parameters are:

- Sludge volume index (SVI)
- Oxygen uptake rate
- Microscopic examination
- Aerator loading

- Detention time
- Mixed liquor DO level

Sludge Volume Index This index is defined as the volume (in milliliters) occupied by one gram of activated sludge mixed liquor solids, dry weight, after settling for 30 minutes in a 1000 mL graduated cylinder. In practice, it is taken to be the percent volume occupied by the sludge in a mixed liquor sample (taken at the outlet of the aeration tank) after 30 minutes of settling, divided by the suspended solids concentration of the mixed liquor. The formula is expressed as:

$$\text{SVI} = V_s/\text{MLSS} \tag{23.11}$$

where SVI = sludge volume index, mL/g MLSS
V_s = volume of settled sludge after 30 minutes, mL/L
MLSS = mixed liquor suspended solids, g/L

SVI has been used as an indication of the settling characteristics of the sludge. However, SVI that is characteristic of good settling sludge varies with the type of industrial waste and concentration of mixed liquor solids, and observed values at a given plant should not be compared with those reported for other plants or in the literature. Typical SVI for good settling sludge with mixed liquor concentrations is in the range of 1500–3500 mg/L are:

- SVI of 80–120 is normal and considered good settling.
- SVI greater than 120 is an indication of possible bulking in the clarifier.
- SVI less than 80 is an indication very compact and heavy floc.

Dissolved Oxygen Uptake DO uptake is determined from a short duration DO test measurement in a standard 300 mL BOD_5 bottle, using oxygen saturated samples of fresh aerator mixed liquor, return sludge, bioreactor influent, or a mixture of bioreactor influent, plus a portion of return sludge. Results are typically taken once or twice a shift by treatment plant operators, and the results are usually graphed.

$$\text{OUR} = (\text{DO}_0 - \text{DO}_{10})(60\ \text{min}/h)/10 \tag{23.12}$$

$$\text{MLRR} = \text{OUR}/\text{MLVSS} \tag{23.13}$$

where OUR = oxygen uptake rate, mg $O_2/(L \cdot h)$
DO_0 = initial DO at time zero, mg/L
DO_{10} = DO after 10 minutes, mg/L
MLRR = mixed liquor respiration rate, mg $O_2/(\text{g MLVSS} \cdot h)$
MLVSS = mixed liquor volatile suspended solids, g/L

Results are typically used to evaluate factors such as aeration system capacity limitations, mixed liquor solids levels, bioreactor raw water treatability, immediate DO demand, reactivity of raw wastes, and return sludge thickening time limits for maintaining viable mixed liquor microorganisms in the secondary clarifier.

The respiration rate tells an operator about the state of health of activated sludge mixed liquor. The respiration rate of a normal steady-state operational activated sludge plant changes from season to season.

Interpretation of these results is straightforward. A typical respiration rate in a sludge sample from the beginning of the aeration tank is between 12 and 20 mg $O_2/(\text{g MLVSS} \cdot \text{h})$. Higher rates indicate high organic loading, while lower rates indicate low loading. Respiration rates higher than normally observed suggest increases in reactor BOD loadings or F/M. High respiration rates [usually more than 35–45 mg $O_2/(\text{g MLVSS} \cdot \text{h})$] are usually characteristic of young mixed liquor that is under oxidized. Comparison of oxygen uptake rate of mixed liquor with that of secondary effluent usually shows high effluent uptake rate [20–30 mg $O_2/(\text{L} \cdot \text{h})$ for secondary effluent is high]. High results should be compared with settling or compaction rates of mixed liquor solids and foaming tendencies, since these results tend to be related when mixed liquor solids are young and under aerated.

Lower than normal respiration rates indicate one of three things:

1. SRT is longer than usual.
2. BOD loading has dropped off, decreasing F/M.
3. Some type of biological inhibitory agent is present in the waste.

Low respiration rate should be checked right away with oxygen uptake results for all four samples. Healthy activated sludge has an oxygen uptake rate of 8 to 20 mg $O_2/(\text{L} \cdot \text{h})$ for a sample of mixed liquor. When levels drop below this range, it can be an indication of biological toxicity in the reactor, dictating the need for specific action.

Mixed Liquor Dissolved Oxygen Mixed liquor DO level in activated sludge aeration basins is controlled by:

- Organic loading directly influences oxygen uptake rate, which indirectly affects DO level.
- Aeration source and level directly influence DO level.
- Mixed liquor solids inventory indirectly influences oxygen uptake rate and F/M ratio, which in turn indirectly affect mixed liquor DO level.

DO levels in the effluent from the aeration tank are generally maintained between 1.0 and 2.0 mg/L or higher, depending on the process.

Nutrient Removal in Activated Sludge

In water environments such as rivers, lakes, and oceans, the most stringent nutrient for algal growth is phosphorous. Therefore, controlling phosphorous in the water environment is the single most effective means to maintain clean water and prevent eutrophication (algae growth). In addition to phosphorous, nitrogen is the next most stringent nutrient, though some algae can fix gaseous nitrogen in air. While there are many forms of nitrogen in terms of oxidation state, ammonia nitrogen is the most readily utilized form for most organisms that contaminate water. In addition, ammonia nitrogen consumes DO and may suffocate fish and higher life forms, when it is biologically oxidized. Both are important, although controlling ammonia nitrogen is given higher priority than controlling nitrate nitrogen.

In biological effluent treatment, some part of phosphorous and nitrogen can be converted to biomass and eventually removed through sludge wastage. Microorganisms treating effluent contain 1.7% phosphorous and 8.7% nitrogen. If SRT and other conditions are properly managed, the majority of ammonia and organic nitrogen can be oxidized to nitrate, which is less harmful to the water environment. Phosphorous and nitrogen removal can be further enhanced biologically using cyclic DO conditions.

Phosphorous Removal

If sludge containing many kinds of different microorganisms is circulated periodically between low anaerobic and high DO conditions, some species that can adapt well in this cyclic DO condition will have advantage over other microorganisms. While most heterotrophic microorganisms can make energy under the oxygen rich environment, some microorganisms [polyphosphate accumulating organisms (PAO)] can make energy without oxygen by hydrolyzing the polyphosphate accumulated in the cell.

If PAO are circulated between DO rich and anaerobic conditions periodically, they accumulate excess phosphorous during DO rich conditions to prepare for the DO scarce conditions. During DO scarce conditions, PAO absorb fatty acids in the liquid phase and store them in the form of polyhydroxybutyrate (PHB), which is used to produce new PAO during DO rich conditions.

Phosphorous accumulation during DO rich conditions is often called “luxury uptake.” Under aerobic conditions, more phosphorous is accumulated by PAO to prepare for anaerobic conditions. Moreover, during anaerobic conditions, PAO have a clear advantage in survival over other microorganisms.

Phosphorous can be also removed chemically. Addition of chemicals to the secondary clarifier for phosphate precipitation is commonly practiced. A mineral salt addition involving Fe^{+3} or Al^{+3} combines with soluble orthophosphate available and precipitates as insoluble metal phosphates. Chapter 24 describes dosages for phosphorus removal by chemical addition. However, adding acid salts of these metals neutralizes alkalinity of waste and drops pH.

Reduction in alkalinity sometimes inhibits biological treatment in the activated sludge process. In addition, formation of a substantial amount of insoluble iron or aluminum hydroxide can increase sludge handling and dewatering costs significantly.

In these cases, where chemical phosphorus removal is intended to take place in activated sludge, tests should be run to see if sodium aluminate can be substituted for acid metal salts of iron or aluminum. Reactions and products of typical phosphorus removal agents for this type of application are summarized in Chap. 24. Solubility of metal salts used in phosphorus precipitation is strongly pH dependent. Figure 24.1 in Chap. 24 shows solubility of iron and aluminum phosphate versus pH.

Nitrogen Removal

Nitrogen removal can be achieved as follows:

$$NH_4^+ \xrightarrow{O_2} NO_2^- \xrightarrow{O_2} NO_3^- \xrightarrow{BOD} N_2(gas)\uparrow \qquad (23.14)$$

Nitrification occurs by autotrophs in aerobic conditions with consumption of DO. All biological processes having oxygen rich stages and long sludge age can oxidize ammonia nitrogen to nitrate as follows:

$$2NH_4^+ + 3O_2 \xrightarrow{\text{Nitrosomonas}} 2NO_2^- + 2H_2O + 4H^+ \qquad (23.15)$$

$$2NO_2^- + O_2 \xrightarrow{\text{Nitrobacter}} 2NO_3^- \qquad (23.16)$$

Denitrification occurs in the absence of free oxygen (anoxic condition). Most heterotrophs can respire with consumption of combined oxygen in the form of nitrate, nitrite, hypochlorite, etc.

$$2NO_3^- + 2H^+ \longrightarrow N_2(gas)\uparrow + H_2O + 2.5O_2 \qquad (23.17)$$

In the first nitrification process [Eqs. (23.15) and (23.16)], autotrophic microorganisms (nitrifiers) oxidize ammonia nitrogen to nitrate with consumption of DO. Then [Eq. (23.17)] nitrate is reduced to nitrogen gas in anoxic tanks, where heterotrophic microorganisms deliver oxygen from combined oxygen sources such as nitrate due to a lack of elemental oxygen.

In terms of kinetics, nitrification is much slower than denitrification. Autotrophs not only grow slower than heterotrophs, but the amount of food for autotrophs (nitrogen) is scarcer than that for heterotrophs (BOD). Autotroph concentration is normally less than 10% of the total bacterial population. Consequently, if SRT is lower than five days, autotrophs rarely build up to a sufficient level due to washout. Moreover, autotrophs are more sensitive to temperature. Nitrification can be severely affected below 50°F (10°C), except in cases where MLSS is very high such as in membrane bioreactor (MBR) processes in which MLSS is around 10 g/L.

Since combined oxygen in nitrate is utilized during BOD oxidation by heterotrophs, a certain amount of BOD is necessary to reduce nitrate. Theoretically, the BOD/TKN ratio should be at least 3.4:1 to denitrify all nitrogen. If the ratio is lower than 3.4:1, nitrogen removal is limited to some extent depending on BOD deficiency. In these cases, a source of carbon such as methanol is added to the denitrification basin.

In the activated sludge process, pH in the aeration basin often decreases below the optimum range (6.5–7.5) mainly due to formation of nitrates during oxidation of TKN (ammonia nitrogen plus organic nitrogen) contained in the influent. In theory, 1 mg nitrogen can consume 3.6 mg alkalinity as $CaCO_3$, if it is not denitrified. However, when denitrification is performed, net acid formation by nitrification can be reduced, and pH can be maintained more easily.

Aerated Lagoons

Aerated lagoons or ponds evolved from facultative stabilization ponds when surface aerators were installed to overcome odors from organically overloaded ponds.

In an aerated lagoon, all solids are maintained in suspension. Aerated lagoons are operated as flow-through activated sludge systems without recycle, usually followed by large settling ponds. Lagoons and stabilization ponds are currently in use in older plants but are out of favor for new construction due to:

- Odors from algae blooms
- Groundwater contamination concerns because they are only clay lined
- Large land area requirements

Seasonal continuous nitrification may be achieved in aerated lagoon systems. The degree of nitrification depends on design and operating conditions within the system and on effluent temperature. Generally, with higher effluent temperatures and lower loadings (increased SRT), higher degrees of nitrification can be achieved.

Significant Operational Control Parameters

Aerated lagoons followed by a clarifier with sludge recycle are very similar to activated sludge systems with respect to operation and control.

An aerated lagoon is usually deeper than a facultative pond. Mechanical or diffused aerators provide most of the DO required and mix lagoon contents. Turbulence levels should be high enough to ensure uniform DO and suspended solids concentrations throughout. The higher the rate of oxygen transfer to the system, the more intense the mixing in the pond, and subsequently, the less pronounced the tendency for sedimentation. Factors that must be considered in the operation of aerated lagoons are similar to those of the activated sludge process and include: biological solids produced SRT, BOD removal, pond mixing, and temperature effects.

Biological Solids

High-rate aerated lagoons can generate 0.6 to 0.7 lb (0.27–0.32 kg) of suspended solids per pound (kilogram) of BOD_5 removed.

Solids Retention Time

The basis of operation for an aerated lagoon is SRT. Typical SRT design values for aerated lagoons used for treating low-strength industrial wastes vary from 3 to 6 days. Aerated lagoons used in paper mills, refineries, and petrochemical plants have SRT of 10 to 20 days; these generally operate in the extended aeration mode.

Biochemical Oxygen Demand Removal

Aerated lagoons that are properly designed operated and maintained, can produce effluent that is low in solids and with effluent BOD_5 of less than 30 mg/L. Solids concentrations in effluent are variable (20–100 mg/L) and are affected by seasonal changes.

pH and Alkalinity Balance

In general, aerated lagoons operate most satisfactorily in the pH range of 7.2 to 7.8. To achieve desired pH, influent waste pH should be maintained from 6.5 to 8.3.

Oxygen Requirement

Based on operating results obtained from a number of industrial and domestic installations, the amount of oxygen required varies from 0.7 to 1.4 times the amount of BOD_5 removed.

Temperature

The two most important effects of temperature are, reduced biological activity and treatment efficiency, and formation of ice.

Icing effects may be minimized by increasing the depth of the lagoon or by altering the method of operation. Reducing the area by one-half increases effluent temperature. This action corresponds roughly to about a 50% increase in the rate of biological activity.

Stabilization Ponds

A stabilization pond (also called an oxidation pond) is a relatively shallow body of water contained in an earthen basin of controlled shape, designed for treating effluent. Ponds in the past were used extensively for treatment of industrial effluent and mixtures of industrial and domestic effluent that are amenable to biological treatment. Installations are now serving such industries as oil refineries, slaughterhouses, dairies, poultry processing plants, and rendering plants. New regulations, which require double lining of effluent lagoons that contain specific toxics such as benzene, will limit continued usage of these systems in the future.

Pond Classification

Stabilization ponds are usually classified according to the nature of biological activity taking place: aerobic, anaerobic, or combined aerobic–anaerobic (facultative). Principal types of stabilization ponds in common use are shown in Table 23.10. Other classification schemes used are based on the type of influent (untreated, screened, settled effluent, or activated sludge effluent); pond overflow condition (nonexistent, intermittent, or continuous); and method of oxygenation (photosynthesis, atmospheric surface reaeration, or mechanical aerators).

Stabilization ponds have been used singly or in various combinations to treat both domestic and industrial wastes. Aerobic ponds are used primarily for treatment of soluble organic wastes and effluents from effluent treatment plants. Aerobic–anaerobic ponds (facultative) are the most common type and have been used to treat domestic effluent and a wide variety of industrial wastes. Anaerobic ponds are especially effective in bringing about the rapid stabilization of strong organic wastes. Usually, anaerobic ponds are used in series with aerobic–anaerobic ponds to provide complete treatment.

Rotating Biological Contactors

A RBC, also known as bio-disc, uses a biological slime of microorganisms, which grow on a series of thin discs mounted side-by-side on a shaft (Fig. 23.8).

This is considered an attached growth biological process. Discs are rotated slowly and are partially submerged in effluent. Discs are usually made of lightweight plastic. The RBC may be covered to protect the process from low temperatures and to reduce odors. When the process is first started, microbes in the effluent begin to stick to disc surfaces and grow there until all discs are covered with a 1/16 to 1/8 inch (1.6–3.2 mm) layer of biological slime. A thin film of effluent and the organisms on the disc get oxygen from air as the disc rotates.

Type of Pond or Pond System	Common Name	Identifying Characteristic	Application
Aerobic (0.5–2 ft) (0.2–0.6 m)	High-rate aerobic pond		Nutrient removal, treatment of soluble organic wastes, conversion of wastes.
Aerobic (2–5 ft) (0.6–1.5 m)	Low-rate aerobic pond	Designed to maintain aerobic conditions throughout the liquid depth.	Treatment of soluble organic wastes and secondary effluents.
	Maturation or tertiary pond	Similar to low-rate aerobic ponds but very lightly loaded.	Used for polishing (upgrading) effluents from conventional secondary treatment processes, such as trickling filter or activated sludge.
Aerobic–anaerobic	Facultative pond	Deeper than a high-rate pond. Photosynthesis and surface reaeration provide oxygen for aerobic stabilization in upper layers. Lower layers are facultative. Bottom layer of solids undergoes anaerobic digestion.	Treatment of screened or primary settled effluent and industrial wastes. Secondary effluent polishing
Aerobic–anaerobic	Facultative pond with mechanical surface aeration	As above, but small mechanical aerators are used to provide oxygen for aerobic stabilization.	Treatment of screened or primary settled effluent and industrial wastes. Secondary effluent polishing

Table 23.10 Types and Applications of Stabilization Ponds

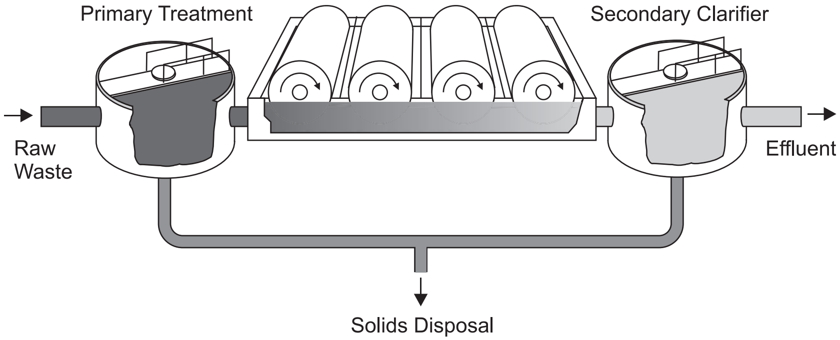

Figure 23.8 Schematic of RBC process.

This film of effluent then mixes with the rest of the effluent, adding oxygen to the treated and partially treated effluent. Excess growth of microbes breaks off from the discs and flows to the clarifier to be separated from the effluent. Rotation of the discs provides fresh media surface for buildup of attached microbial growth, brings growth into contact with effluent, and aerates effluent and growths in the effluent reservoir. The attached growth is like the growth in a trickling filter, except that microbes are passed through effluent rather than effluent passing over microbes. The process can achieve secondary effluent quality or better. By placing several sets of discs in series, it is possible to achieve even higher degrees of treatment, including biological conversion of ammonia to nitrate (nitrification).

The RBC system design is based on disc surface area and percent BOD and ammonia removal efficiency. Common loading rates for secondary treatment of municipal effluents are 2 to 4 gpd/ft^2 [0.08–0.16 m^3/(d · m^2)] of effective media area. At temperatures above 59°F (15°C), 90% nitrification can be obtained at loadings of 1.5 gpd/ft^2 [0.06 m^3/(d · m^2)].

Trickling Filters

A trickling filter consists of a bed of coarse material, such as stones, slats, or plastic, over which effluent is discharged from moving spray distributors or fixed nozzles. A secondary clarifier usually follows a trickling filter to reduce effluent suspended solids. Sometimes, trickling or high-rate filters are used as a first stage treatment for high BOD effluents, followed by an activated sludge system. Figure 23.9 shows a trickling filter and its principal components, which include:

- Distribution system, which applies effluent to filter media
- Filter media, which provides surface area for microorganisms to grow

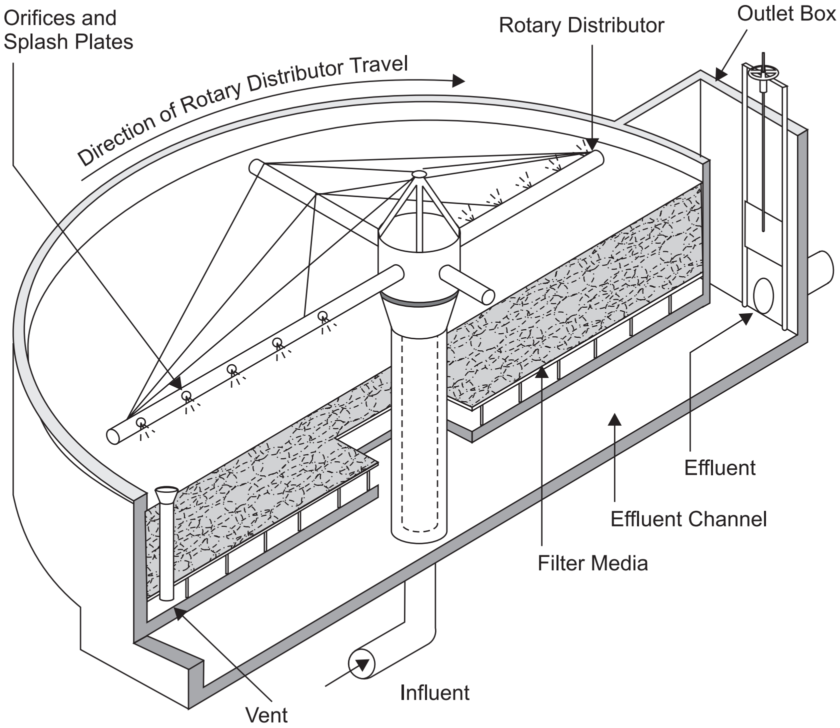

Figure 23.9 Trickling filter cross section.

- Under drain system, which supports the media and provides drainage of waste flow to a collection channel, while permitting air circulation up through the media to supply oxygen to microorganisms

The rotary distributor is used to prevent growth of flies that were common in older designs using pipe headers and nozzles. Distributors are rotated by reaction of the discharge of water through orifices on the distributor arms.

Principles of Operation

Trickling filters are not a filtering or straining process as the name implies. The rocks in a rock filter are 1 to 4 inch (25–102 mm) in diameter, too large to strain solids (Fig. 23.9). Filters provide large amounts of surface area where microorganisms cling and grow in slime on rocks as they feed on organic matter. Excess growths of microorganisms wash from the rock media and would cause high levels of suspended solids in the plant effluent if not removed. Thus, flow from the filter is passed through a secondary clarifier to allow these solids to settle.

There are several ways to prevent biological slimes from drying out and dying when effluent flows are too low to keep the filter wet. One method is to recycle filter effluent. Recirculation reduces odor potential and improves filter efficiency as it provides another opportunity for microbes to consume organics that escaped the first pass through the filter. Another approach to improve performance or handle strong effluents is to use two filters in series, referred to as a two-stage trickling filter system.

Synthetic media for trickling filters have recently become popular. These materials include modules of corrugated plastic sheets, redwood slats, and plastic rings. These media offer larger surface areas for slime growths, typically 27 ft^2 (2.5 m^2) surface area per cubic foot (0.028 m^3) as compared to 12 to 18 ft^2 (1.1–1.7 m^2) per cubic foot (0.028 m^3) for 3 inch (76 mm) rocks, and greatly increase void ratios for increased airflow. The materials are also much lighter than rock (by a factor of about 30), and trickling filters can be much taller without structural problems. While rock in filters is usually not more than 10 ft (3 m) deep, synthetic media depths are often 20 ft (6.1 m) or more, reducing overall space requirements for the trickling portion of the treatment plant. Molded plastic media use pieces of interlocking corrugated sheets of plastic that look like a honeycomb. Sheets are stacked so that they interlock and fit inside the filter structure.

Sludge Reduction Process

Biological effluent treatment processes always result in generation of a considerable amount of excess sludge that has to be wasted. In general, 0.5 to 0.6 lb (kg) dry sludge is produced when 1 lb (kg) BOD is treated. The expense for excess sludge treatment has been estimated at 40 to 60% of the total expense of effluent treatment. Moreover, the conventional disposal method of landfilling may cause secondary pollution problems. In areas where landfilling of sludge is restricted, sludge disintegration methods have an economic benefit and fit in the market. However, in areas where sludge disposal options are still relatively inexpensive, sludge disintegration techniques are not readily employed due to additional costs of equipment and operation.

Overall process efficiency can be measured by the ratio of soluble COD divided by total COD. Another way to measure efficiency is to determine the amount of disintegrated solids divided by total sludge solids. At the time of this writing, there are different methods used for this calculation, and there is no apparent universally accepted method as different authors use different calculations.

Sludge reduction can be achieved by inserting sludge disintegration devices in most biological effluent treatment processes as shown in Fig. 23.10. In this process, some part of return sludge thickened in the clarifier is sent to a sludge disintegrator to solubilize the sludge.

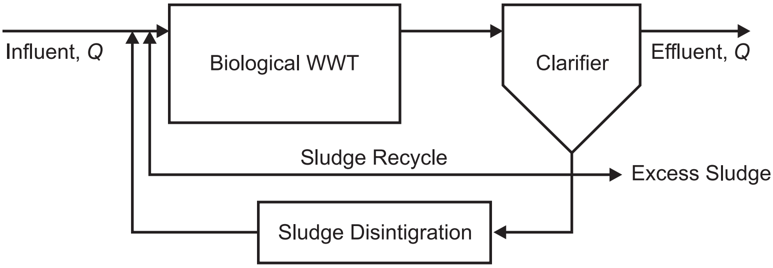

Figure 23.10 Schematic of basic concept of sludge reduction process.

Solubilized sludge that contains soluble BOD and cell debris is sent back to the bioreactors, where live microorganisms consume the BOD and cell debris. Since only about 60% of carbon contained in disintegrated sludge is converted to new microorganisms while about 40% turns to carbon dioxide, net sludge reduction can be readily achieved.

In principle, all kinds of chemical, mechanical, and biological methods that kill microorganisms can be used for sludge disintegration. While ozone is most commonly used at a dosage of 0.02 to 0.10 g O_3/g TSS, ball mill, microwave, ultrasound, electrolysis, and alkaline/acid treatments can be also used for sludge disintegration. In some commercial processes, biological methods such as thermophilic reactors and anoxic selectors are used for sludge disintegration. In thermophilic processes, part of return sludge is sent to a high-temperature aerobic reactor that is operated at 140 to 158°F (60–70°C). In this high-temperature condition, the majority of microorganisms contained in return sludge die, and the debris is used to grow thermophilic microorganisms, which die again after recycled to the aeration basin. An identical logic is used for an anoxic selector.

Accumulation of inert materials in sludge can affect overall efficiency significantly. Since about 8% of cell mass is nonbiodegradable in aeration basin conditions, inert material can accumulate, if the sludge disintegrator does not convert it to biodegradable materials. In this case, the portion of biologically active solids in MLVSS increases and the actual F/M ratio goes up. To maintain proper biological activity in sludge, some excess sludge removal is inevitable. However, if the disintegration process is efficient in converting nonbiodegradable materials to biodegradable materials, excess sludge removal can be minimized. In general, chemical sludge disintegration methods have an advantage over mechanical methods in terms of inert material accumulation.

It is known that nitrogen removal is hardly affected by sludge disintegrators, if anoxic reactors are simultaneously used with the aeration basin and disintegrated sludge is supplied to the anoxic tank. It is because the denitrification rate is boosted by additional

BOD supplied from the sludge disintegrator. However, phosphorous removal efficiency decreases, since phosphorous removal relies solely on the amount of sludge removal.

Anaerobic Systems

Most of the discussions so far have been about aerobic biological treatment processes. This section addresses anaerobic treatment processes.

Anaerobic Sludge Digestion

Anaerobic digestion is one of the oldest processes used for stabilization and reduction of domestic primary and biological sludges. Typically, it is not used in industrial effluent treatment systems. In the process, organic material in sludge is converted biologically to a variety of end products, including methane (CH_4) and carbon dioxide (CO_2), under anaerobic conditions.

The process is carried out in an airtight reactor with sludge introduced and removed on an intermittent basis. There are two basic types of sludge digestion systems: standard rate and high rate. In the standard rate system, reactor contents are unmixed and unheated. The detention time is 60 to 90 days.

The reactor for the high-rate process is completely mixed and heated to 85 to 100°F (29–38°C), resulting in a typical detention time of 15 days or less. The most common configuration is the two-stage system, in which the first stage is heated and mixed. The second stage reactor is not mixed or heated and is allowed to stratify to remove concentrated digested sludge, supernatant liquor, and methane gas. Generally, a scum layer develops on the surface of the liquor in domestic systems. The resulting sludge is well stabilized, and total solids are reduced 45 to 50% by weight. Methane produced is used to heat the digester, heat buildings, generate electricity, or drive mechanical equipment such as pumps and blowers.

Anaerobic Treatment

The anaerobic treatment process involves decomposition of organics in effluent to methane and carbon dioxide in the absence of oxygen. Process kinetics and material balances are similar to aerobic systems, but there are certain basic differences that require consideration. Conversion of organics to methane gas yields little energy, so that the rate of cell growth is slow and the quantity of organic growth is low. Thus, the rate of treatment and sludge solids yield are both considerably less than in the activated sludge process.

The anaerobic treatment process is used for treating effluents that have high organic content. Among these industries are meatpacking, breweries, alcohol production, pharmaceutical, various types of food

Effluent Source	BOD, mg/L	COD, mg/L
Sugar	50–500	250–1500
Dairy	150–500	250–1200
Maize starch	—	500–1500
Potato	200–300	250–1500
Vegetable	100	700
Wine	3500	—
Pulp	350–900	1400–8000
Fiber board	2500–5500	8800–14 900
Paper mill	100–200	280–300
Landfill leachate	—	500–4000
Brewery	—	200–350
Distillery	—	320–400

Table 23.11 BOD and COD in Anaerobic Treatment Effluents

processing, pulp and paper, and oilfield produced water. Influent BOD and COD in some effluents being treated are very high, such as alcohol stillage with 40 g/L BOD and 120 g/L COD. The anaerobic process may be the sole treatment, or it may be ahead of an aerobic treatment system, depending on treated water discharge requirements. Typical organic removals are 75 to 95%, depending on design and application. Table 23.11 illustrates the BOD/COD characteristics from anaerobic treatment of various effluents.

Advantages and disadvantages of the anaerobic treatment process as compared to aerobic systems relate directly to the slow growth rate of organisms in anaerobic systems. Slow growth rates mean that reactor detention times have to be relatively long for high efficiency. Slow growth also means that only a small portion of organic material is synthesized into new cells. This means there is a minimal amount of sludge for disposal. A sufficient amount of nutrients must be present, just as in aerobic systems. The amount of nutrients is substantially less than in aerobic systems due to the low growth rate. Most organics are converted to methane that is a useful, combustible product.

Process

Four groups of microorganisms sequentially degrade organic matter in anaerobic fermentation. Hydrolytic microorganisms degrade polymer-type material such as polysaccharides and proteins to monomers. This reaction results in no COD reduction.

Monomers are then converted into fatty acids by acid-forming bacteria with a small amount of hydrogen (H_2). Principal acids are acetic, propionic, and butyric. In the acidification stage, there is minimal reduction of COD. Should a large amount of H_2 occur some COD reduction occurs? This seldom exceeds 10%.

All acids higher than acetic acid are converted to acetic and H_2 by acetogenic microorganisms. The conversion of propionic acid is:

$$C_3H_6O_2 + 2H_2O \rightarrow C_2H_4O_2 + CO_2 + 3H_2 \tag{23.18}$$

In this reaction, COD reduction does occur in the form of H_2.

Acetic acid and H_2 are converted to methane by methanogenic organisms (methane formers):

Acetic acid:

$$C_2H_4O_2 \rightarrow CO_2 + CH_4 \tag{23.19}$$

$$CH_3COO^- + H_2O \rightarrow CH_4 + HCO_3^- \tag{23.20}$$

Hydrogen:

$$HCO_3^- + 4H_2 \rightarrow CH_4 + OH^- + 2H_2O \tag{23.21}$$

The kinetic relationship commonly employed for anaerobic degradation is the Monod relationship:

$$\mathrm{ds/dt} = K_{\max} SX/(K_S + S) \tag{23.22}$$

where $\mathrm{ds/dt}$ = substrate (COD) utilization rate, mg/(L·d)
$K_{\max}$ = maximum specific substrate utilization rate, g COD/(g VSS·d)
S = effluent COD concentration, mg/L
X = biomass concentration, mg/L
K_S = half saturation concentration, mg/L

One pound (0.45 kg) of COD or ultimate BOD_L removed in the process yields 5.62 ft^3 (0.16 m^3) of methane at standard conditions [32°F (0°C) and one atmosphere] and 6.3 ft^3 (0.18 m^3) at 35°F (1.7°C). Low BOD and COD effluents may not produce enough gas to heat the reactor. Conversely, high strength wastes produce excess gas that is used as a source of energy such as heat and electricity. Coefficients for Eq. (23.22) are shown in Table 23.12.

Temperature, °F (°C)	$K_{\max}$, d^{-1}	K_S, mg/L
95 (35)	6.67	164
77 (25)	4.65	930
68 (20)	3.85	2130

Table 23.12 Typical Coefficient Values for Monod Relationship

Actual organic loading to the reactor depends on reactor design and type of waste. Bench and pilot tests have to be conducted, if the supplier of the anaerobic system has not had prior experience on the type of waste. Startup of an anaerobic system can take anywhere from a few months to nine months or more, depending again on the type of organic waste. Seed sludge taken from a similar application reduces startup time.

Membrane Bioreactors

Use of MBR has expanded considerably, from a few systems in the 1980s to several thousand in 2005. In these systems, ultrafiltration (UF) or microfiltration (MF) membranes replace sedimentation basins for separation of biomass from water.

MBR Process

The membrane can be installed in the bioreactor tank or in an external tank, where biomass is continuously separated from water. Since solids–liquid separation is performed by a membrane, lower effluent TSS can be achieved compared to a conventional settling basin. More importantly, MBR decouples the biological process from the process of settling biomass. This allows operation of the biological process at conditions that would be untenable in a conventional system, including high MLSS of 8 to 15 g/L, long SRT, and low hydraulic retention time. In conventional systems, such conditions could lead to sludge bulking and poor settleability.

The MBR process replaces the conventional clarifier with membranes, which can be submerged directly in the aeration basin or reside in an external tank. These microporous membranes have a pore size range between 0.04 and 0.4 μm and allow for almost complete particle separation from mixed liquor. MBR have the following benefits:

- MLSS can be increased to 8 to 15 g/L (versus 1.5–8 g/L for conventional systems)
- Higher MLSS can reduce HRT
- Lower sludge production
- Lower effluent TSS
- Lower effluent BOD
- Up to 50% footprint reduction
- Higher SRT can produce good nitrification

A conventional system is shown in Fig. 23.11, while the MBR system is shown in Fig. 23.12. Membranes serve as the separation device for solids–liquid separation instead of a clarifier or dissolved

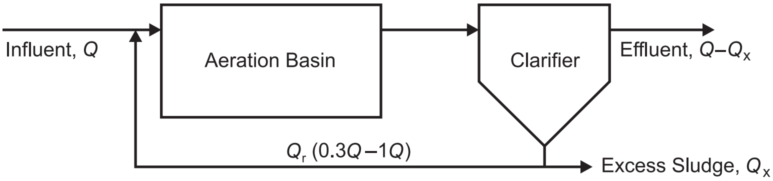

FIGURE 23.11 Conventional activated sludge process.

air flotation (DAF) unit. Membranes are used in this submerged configuration and operated under vacuum, or they are used external to the aeration basin and operated under pressure. In a submerged MBR (sMBR), a suction pump is used to pull clean water through the membrane, while excluding passage of particles. In an external MBR (eMBR), a recirculating pump is used to deliver mixed liquor under pressure to the membranes and then back to the aeration basin.

In sMBR, air bubbles are released directly underneath the membranes, and this provides the shear forces necessary to minimize solid particle build-up on the membrane surface. The main operating variables used to maintain flow across the membrane surface (flux) are the aeration rate and suction pressure, which is the driving force that controls the amount of water transported across the membranes, and is directly related to flux. Cross-flow velocity is the main operating variable that controls flux in eMBR.

In addition, to further maintain flux, both systems depend on intermittent operation. During the off cycle, the membrane surface continues to be scoured by water and air, and solid debris is loosened and removed. In some membrane systems using hollow fibers, a periodic back pulse of permeate is used to help remove accumulated solids. Membranes can be taken out of service and cleaned chemically with sodium hypochlorite, caustic, or organic acids.

Membranes are constructed of polymeric or ceramic materials. The vast majority of membrane systems are made from polymeric materials such as polyvinylidine difluoride, polyethylene, and chlorinated polyethylene. Membrane geometry is usually either hollow fiber or flat sheet (Figs. 23.13 and 23.14).

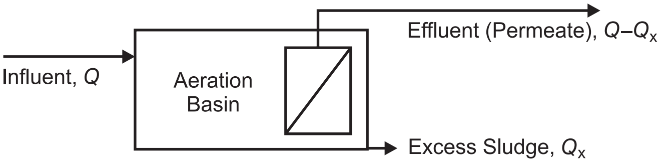

FIGURE 23.12 MBR process.

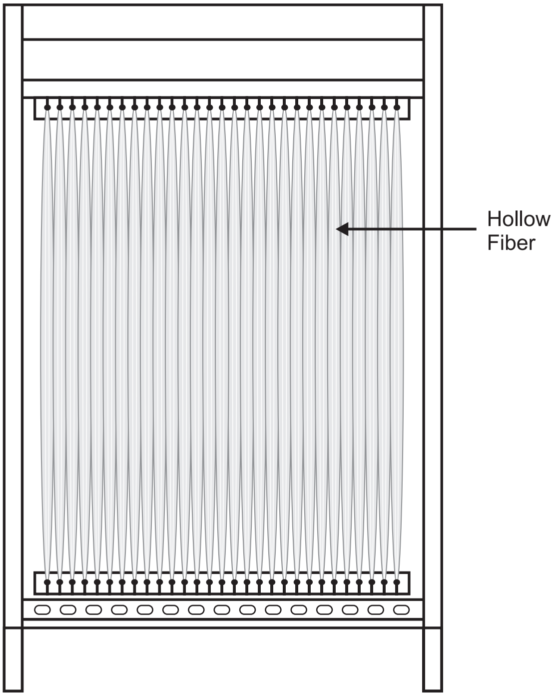

Figure 23.13 Hollow fiber MBR membrane configuration.

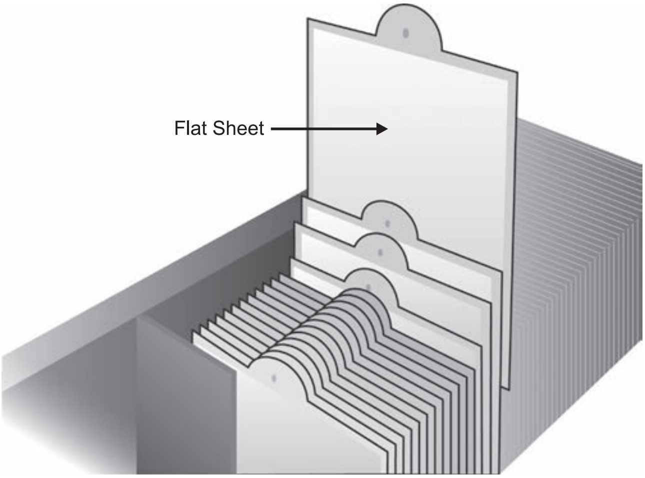

Figure 23.14 Flat sheet membrane configurations.

In hollow fiber and flat sheet membranes, water flow is from the outside to the inside. Pore openings can range from the UF to the MF size. Key operational variables are flux, transmembrane pressure (TMP), and membrane aeration rate.

Gross flux is calculated from Eq. (23.23):

$$\text{Flux}_\text{G} = F/A \tag{23.23}$$

where Flux_G = gross flux, gal/(h · ft^2) [L/(h · m^2)]
F = flow rate, gph (L/h)
A = membrane area, ft^2 (m^2)

The net flux is the gross flux minus the time required for relaxation, during which there is no water flow and is given by Eq. (23.24):

$$\text{Flux}_\text{N} = \text{Flux}_\text{G}(100 - \text{Relax\%})/100 \tag{23.24}$$

where Flux_N = net flux, gal/(h · ft^2) [L/(h · m^2)]
Relax% = time required for relaxation, %

MBR Limitations

Use of MBR is growing worldwide at a rate of 25 to 30% per year. Driving this growth rate is the many advantages of MBR over conventional effluent treatment processes. However, membrane fouling is the one problem that is limiting even greater expansion, and is causing many operational issues at existing MBR plants. Various approaches have been tried to reduce membrane fouling, such as intermittent suction, back flushing, module design improvement, and optimization of aeration. Combinations of these methods have reduced costs of MBR significantly, but further improvements are possible.

Membrane fouling is directly related to condition of the biomass. Although MBR do not have to operate under conditions to form settleable floc such as in a waste activated sludge system, certain operating conditions tend to generate more foulants and make membranes more susceptible to fouling and flux loss. Reasons why these foulants form are complex and not completely understood. However, frequent changes in influent feed water quality, lack of equalization, frequent peak flow events, insufficient DO, and poor control of MLSS concentration are contributing factors that tend to generate more foulants and increase membrane fouling. These factors are all interlinked to the operating parameters of the MBR such as HRT, SRT, and percent MLSS. The main objective of any MBR is to obtain long-term sustainable flux and good water quality under normal and peak flow conditions, and to accomplish this at minimum cost.

Microbial Foulants

Soluble microbial products (SMP) are major membrane foulants in the MBR processes. SMP consist of soluble polysaccharides and protein biopolymers that are produced by microbial organisms. This material is released when microbial cells lyse. SMP material along with other submicron particles can deposit on membrane surfaces and restrict flow of water through the membrane. If particles are smaller than the membrane pore size, this material can block the pores and irreversibly foul the membrane surface. Irreversible foulants cannot be removed by the techniques described above, but instead, membranes must be taken off-line and cleaned by submersion and soaking in various cleaning solutions, such as bleach, acids, and caustic. Even this aggressive cleaning sometimes fails to remove foulants. Irreversible fouling is the most significant contributor to reduced membrane life.

SMP material that is larger than the membrane pore size can coat the surface of the membrane and form a gel layer. This layer can actually help prevent particles that are smaller than membrane pores such as viruses from passing through the membrane into the effluent water. However, if this gel layer becomes too thick, there is often increased resistance that reduces membrane flux.

After membranes are cleaned using cleaning methods recommended by the supplier of the membranes, filtration rate and membrane pump pressures are monitored to determine the extent of membrane filtration improvement. The cleaning process should have brought the membrane performance back to design conditions. If not, then significant fouling has occurred, and either additional cleaning or replacement of membranes could be required.

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CHAPTER 24

Tertiary Effluent Treatment

The main objective of tertiary effluent treatment is removal of ammonia, phosphorous, and suspended solids, and the purification of secondary effluent to a level sufficient for discharge into the environment. Secondary effluent treatment processes typically remove over 90% of the biochemical oxygen demand (BOD), suspended solids, and a variety of other pollutants. Sometimes, additional removal of excess ammonia, phosphorus, and organics is required to meet discharge permits.

Requirements for water discharge vary by location and by industry. Thus, industry-specific requirements may require special treatments to address specific issues. However, many industries have similar issues with effluent ammonia, phosphate, and solids. For example, excess ammonia nitrogen can cause toxicity issues, while excess phosphate can cause algae blooms in receiving waters. Algae blooms can consume dissolved oxygen in the receiving water and result in fish kills. Excess BOD can cause bacterial blooms as well. Thus, tertiary treatment processes are specifically designed to follow a secondary (biological) waste treatment system, and ensure reduction in ammonia, phosphate, and other pollutants to meet permit requirements, and ensure protection of the environment.

Specific operations and processes applicable to tertiary effluent treatment can be classified as physical or chemical, and the actual treatment is often a combination of both. Selection of a given operation or process depends on end use of treated effluent, nature of the effluent, and suitability of the various operations and processes to achieving the goals.

The most common tertiary effluent treatment goals are as follows:

- Disinfection through chemical or mechanical means
- Dechlorination for water discharge

- Solids removal
- Ammonia reduction
- Phosphate reduction
- Organics removal

Disinfection

Disinfection of effluent can be achieved through chemical and mechanical means. The disinfection process has the goal of killing microorganisms in water to ensure suitability of the water for entry into the environment. The disinfection process not only must provide a sufficient kill of microorganisms but also provide a residual effect to maintain control over the microbial population. A disinfection process should control and prevent pathogenic bacteria from growing and recontaminating the water.

Mechanical or physical disinfection processes include ultraviolet light, radiation, and heat. While these treatments can kill bacteria, none have a residual effect, and the bacteria can recontaminate water after treatment. Thus, mechanical treatment is often followed by chemical treatment that has disinfection persistence in water. The more common chemical treatments include chloramines, bromine, iodine, hydrogen peroxide, chlorination with chlorine gas or bleach (sodium hypochlorite), and in some cases ozone and chlorine dioxide. Use of ozone and chlorine dioxide is less common because as a gas they tend to flash off and do not provide long-term microbial control. Chlorination is the most common disinfection practice due to the extensive knowledge of how it works, industry wide acceptance of the practice, and overall lower cost.

In some special cases, ozone combined with ultraviolet light is used to maintain bacterial control in critical process waters where halogens are undesirable. In these systems, ozone provides bacterial control, and ultraviolet light is used to destroy the ozone before the water is used. While this is not an extremely common effluent treatment practice, ultraviolet light is being used to disinfect effluent, and developments are being made in ultraviolet light technology that may promote further use in the future.

Chlorination

Chlorination is widely practiced in municipal effluent treatment because of regulations requiring disinfection of effluent effluents. Chlorination can be used to disinfect effluent treatment effluents, convert ammonia in the waste flow to other nitrogen compounds, stabilize sludge (chlorine oxidation), and oxidize some heavy metals to an insoluble form. For disinfection, chlorine concentration and contact time dictate the process for achieving acceptable results. The range of typical chlorine dosages for various types of effluents is shown in Table 24.1. Contact time can vary depending on the situation.

Waste	Chlorine Dosage, mg/L
Raw sewage	6–12
Raw sewage (septic)	12–25
Settled sewage	5–10
Settled sewage (septic)	12–40
Chemical precipitation effluent	3–10
Trickling filter effluent	3–10
Activated sludge effluent	2–8
Sand filter effluent	1–5

Table 24.1 Typical Effluent Chlorination Dosage Ranges

For example, at least 1 mg/L residual needs to be maintained for at least 15 minutes for disinfecting sand filter effluent. Higher dosage and longer contact time are required for disinfecting raw sewage.

Chlorination Processes in Effluent Treatment

In biological treatment processes, chlorination is probably the most widely applied process unit operation encountered involving chemical addition. In the United States, chlorination processes are readily instrumented with dosage dependent on the objective. Facilities required for this process are usually simple. Effluent from a treatment plant flows into a mixing tank and contacts chlorine as a solution or gas. Chlorine reacts with water according to the two-step reaction:

1. Hydrolysis:

$$Cl_2 + H_2O \rightarrow HCl + HOCl \tag{24.1}$$

2. Dissociation:

$$HOCl \rightarrow H^+ + OCl^- \tag{24.2}$$

Generation of hydrogen ions (H^+) can lower the pH of water treated with gaseous chlorine, when water alkalinity is too low to buffer the acidity created. In processes where removal of ammonia is intended (breakpoint chlorination), the dosage of gaseous chlorine is usually high enough to require some form of caustic addition.

Dechlorination

Dechlorination of chlorinated effluent is required in many places to protect aquatic biota in the receiving stream. Dechlorination is a very fast reaction and easily accomplished using:

- Activated carbon
- Sodium metabisulfite ($Na_2S_2O_5$)
- Sodium thiosulfate (hyposulfite) ($Na_2S_2O_3$)

- Sulfur dioxide (SO_2)
- Sodium sulfite (Na_2SO_3)

Sulfite (SO_3^{-2}), from either gaseous SO_2, or solid or liquid sodium salts (sulfite, metabisulfite, or thiosulfate), is the most common reducing agent for dechlorination of effluent plant effluents. These reducing agents also work for destroying other oxidizers such as peroxide. Design of gaseous SO_2 equipment and facilities is essentially the same as that of gaseous chlorine facilities, the exception being that special attention must be given to the SO_2 supply system, because of its low vapor pressure. As with all chemical additions, complete mixing with the effluent before discharge must be assured.

Disinfection By-products

Disinfection by-products are formed from the reaction of an oxidant such as chlorine with organic matter in water. Identification of these compounds is very difficult because of the wide variety of naturally occurring organics and extremely low concentration at which they are present. Several chlorinated organics have been identified because of chlorinating water: chloroform and trihalomethanes. Formation of these chlorinated organics appears to be related to the type of disinfectant chemical used, dosage, and reaction time. Chlorinated by-products may be formed directly or because of the breakdown of other disinfection by-products. Control of chloroform and trihalomethanes can be accomplished by controlling the type of disinfectant chemical used, dosage, and reaction conditions. Often, chlorinated organics do not pose an issue with effluent discharge due to very low concentrations. However, if effluent is to be reused or recycled, there may be a concern depending on the end use of the water.

Solids Removal

Excess suspended solids can require additional treatment by settling and filtration. These processes are the same as those used for primary and secondary effluent treatment. See Chap. 6 for detailed descriptions of clarification and filtration processes.

Ammonia Reduction

Nitrogen in its many forms has long played a fundamental role in the aquatic environment. In certain forms, ammonia nitrogen is one of the major nutrients supporting blooms of green and blue-green algae in surface waters. Ammonia not only has microorganism nutrient value, but can represent as much as 70% of the total oxygen demand of conventionally treated municipal effluent.

During conventional biological effluent treatment, almost all nitrogen contained in effluent is converted into ammonia nitrogen. Although ammonia has very little toxicity to humans, treated effluent containing ammonia has several undesirable features:

- Ammonia consumes dissolved oxygen in the receiving water.
- Ammonia can be toxic to fish life.
- Ammonia increases the amount of chlorine required for disinfection.

Ammonia nitrogen levels can be reduced or removed from effluent by either biological or physical–chemical methods. Biological treatment processes are discussed in Chap. 23. The physical–chemical category can be further divided into: ammonia stripping, selective ion exchange, and breakpoint chlorination.

Ammonia Stripping

Alkaline effluent can be pumped to the top of a cooling tower and distributed over the fill. Air is drawn through media to extract ammonia from water droplets. The simplicity of the process makes it the least expensive method of removing ammonia; however, ammonia is simply transferred to air, where there could be issues with air quality. During warm weather, air stripping can achieve 95% removal of ammonia at pH 11.5 by using 400 ft^3 of air per gallon of effluent (3 m^3 of air per liter of effluent). Cold weather adversely affects performance, and prolonged periods of freezing weather render the process inefficient and often inoperable.

Scale formation is a serious operating problem in full-scale ammonia stripping towers. If soft scale formation is anticipated, a water spray system can be installed to keep soft scale from accumulating. If scaling results in hard deposits, spraying is not likely to eliminate the problem. Scale inhibitors and threshold treatments can be effective in preventing hard scale formation.

Selective Ion Exchange

In this process, ammonium ions in solution are exchanged for sodium or calcium ions displaced from an insoluble exchange material. The process operation resembles that of a water softener, except that the material being removed is ammonium ion rather than water hardness. Both are ion exchange processes.

The selective ion exchange process derives its name from use of ion exchange material that selectively removes ammonia. The process is very efficient and can remove 95 to 97% of the ammonia. However, it is not particularly effective at removing other forms of nitrogen that might be present. Regeneration waste contains ammonia and needs to be handled further before disposal.

Breakpoint Chlorination

In this process, chlorine is added to effluent to satisfy the chlorine demand, so that further addition of chlorine results in directly proportional chlorine residual. Breakpoint chlorination is used for ammonia removal because chlorine, when added to effluent containing ammonia, reacts to form compounds that are oxidized to nitrogen gas. To achieve conversion, about 10 mg/L of chlorine must be added per mg/L of ammonia. Actual dosages are higher due to other compounds in water, which consume some of the chlorine. The overall reaction is:

$$3Cl_2 + 2NH_3 \rightarrow N_2 + 6HCl \tag{24.3}$$

A typical secondary effluent ammonia concentration of 20 mg/L requires about 1700 pounds of chlorine per million gallons treated (200 kg/1000 m^3)—about 40 to 50 times more than normally used in an effluent plant for disinfection only. Reducing organics and solids in effluent reduces the amount of chlorine needed to reach breakpoint. The breakpoint process can result in over 99% removal of ammonia, reducing concentrations to less than 0.1 mg/L (as N). Breakpoint chlorination is typically a very expensive method of ammonia removal, and for this reason, biological treatment processes are typically used instead.

Phosphate Removal

Phosphate is required in secondary effluent treatment plants to maintain healthy biomass for efficient BOD reduction. Typically, 0.5 mg/L phosphate residual in the aeration basin effluent is required to ensure biomass health. Although this level is sufficiently low for most surface water discharge requirements, there is a general trend in regulations to require lower levels. Thus, tertiary treatment for phosphate removal involves precipitation of orthophosphate with metallic ions such as aluminum, iron, and calcium. Polyphosphates and organic phosphates do not readily react with metallic ions, and are removed only after conversion to orthophosphate by biological treatment and hydrolysis, followed then by chemical precipitation. However, small amounts of polyphosphates and organic phosphates may be removed through absorption on floc solids formed by precipitation products of metal ions.

Aluminum Treatment

Aluminum compounds for phosphate precipitation include alum, sodium aluminate, and the various polyaluminum chloride (sulfate) products available in the marketplace. Aluminum ions combine with orthophosphate ions to form aluminum phosphate, which precipitates as follows:

$$Al^{+3} + PO_4^{-3} \rightarrow AlPO_4 \tag{24.4}$$

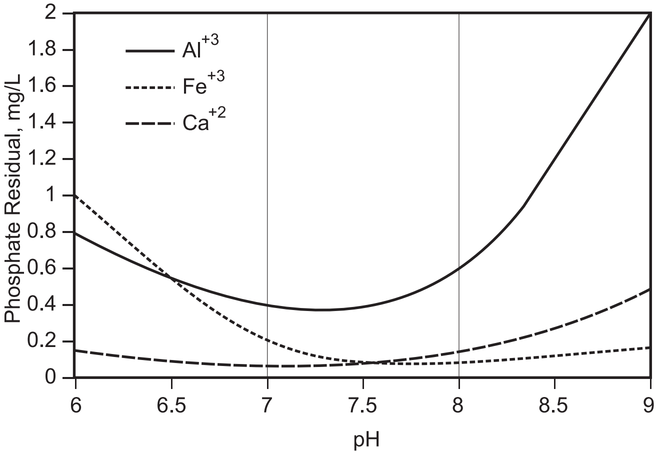

Figure 24.1 Solubility of metal phosphates versus pH.

The solubility of aluminum phosphate compounds is shown as a function of pH in Fig. 24.1. This solubility curve applies to the use of aluminum sulfate (alum) as well as sodium aluminate.

Main factors that affect the actual quantity of alum required to attain a specific orthophosphate concentration include, alkalinity and final pH of effluent. In addition, ionic constituents such as sulfate, fluoride, and sodium, quantity and nature of suspended solids, microorganisms, intensity of mixing, and other physical conditions in the treatment facility may affect overall efficiency of phosphate removal. Optimum pH for precipitation of metal phosphate using alum ranges from 5.5 to 6.5, with 6.0 being best. When running tests or in the full-scale application, it is best to adjust water pH to a value where once the chemical treatment is added, final pH is as close to 6.0 as possible. This reduces formation of aluminum hydroxide and maximizes aluminum phosphate formation and precipitation.

Iron Treatment

Both ferrous (Fe^{+2}) and ferric (Fe^{+3}) ions can be used in precipitation of orthophosphate. Common sources of iron are ferric chloride ($FeCl_3$), ferrous chloride ($FeCl_2$), ferric sulfate [$Fe_2(SO_4)_3$], ferrous sulfate ($FeSO_4$), and pickle liquors (a waste product from metal finishing mills). Ferric is typically most effective in removing orthophosphate when the pH ranges from 4.5 to 6, while ferrous is typically more effective in a pH range of 7 to 8. When testing or in the actual application, it is best to adjust the water pH to a point where once treatment chemical is added, the desired final pH is obtained. This helps maximize precipitation of ferric phosphate and minimize formation of ferric hydroxide.

Iron precipitates phosphate as follows:

$$\mathrm{Fe}^{+3} + \mathrm{PO}_4^{-3} \rightarrow \mathrm{FePO}_4 \qquad (24.5)$$

$$3\mathrm{Fe}^{+2} + 2\mathrm{PO}_4^{-3} \rightarrow \mathrm{Fe}_3(\mathrm{PO}_4)_2 \qquad (24.6)$$

Calcium Treatment

Calcium ions react with orthophosphate ions in the presence of hydroxyl ions to form hydroxyapatite, a form of calcium phosphate. Calculating an approximate dosage for phosphorus removal is possible using mass balance, as was done for alum. However, it is generally not necessary because lime dose is largely determined by alkalinity reactions, similar to those in lime softening that take place when pH is increased.

Reaction of lime with phosphate is pH dependent, and the largest fraction of phosphate can be removed where solubility of hydroxyapatite is lowest (pH about 7). In lime treatment of effluent, operating pH is often determined by the pH required to obtain good suspended solids removal, and as long as the pH does not exceed 9.0, good phosphate removal generally follows.

The total amount of lime sludge generated is more than 2.25 times the amount when sodium aluminate is used for phosphate removal.

Organics Removal

The principal uses of activated carbon as a tertiary treatment process are removal of objectionable organics from effluent and removal of chlorine residual. Both granular activated carbon (GAC) and powdered activated carbon (PAC) can be used. Activated carbon removes organics that are not degraded in conventional biological treatment systems. These refractory organics can be herbicides, lignins, tannins, ethers, or other such compounds. Partitioning of these organics between the water and activated carbon is based on their water solubility. Very soluble organics such as methanol are not removed by activated carbon. In addition, insoluble organics that are in water as an emulsion are difficult to remove.

There are currently two approaches for the use of activated carbon in effluent treatment. One approach is to use GAC in a tertiary treatment sequence following conventional primary and biological secondary treatment. This involves treating secondary effluent by contacting with GAC in fixed beds (columns). Adsorption of residual organics and further BOD and chemical oxygen demand (COD) removal takes place. GAC may be regenerated off site with a loss of about 5% per cycle. Regenerated GAC usually costs about half as much as virgin GAC, and is more generally used in effluent treatment.

The second approach utilizes PAC in a physical–chemical treatment (PCT) process, in which PAC is added directly to the secondary clarifier or biological treatment unit. Although exact mechanisms are not fully understood, bench tests and pilot studies have shown that PAC has positive effects in biological systems. By adsorbing toxic substances and by concentrating feeding sites for bacteria, activated sludge solids retention times tend to increase, thereby effectively reducing treatment costs and counterbalancing the otherwise increased cost for PAC. Regeneration of the dewatered PAC-biosolids mixture is not economically justifiable, and it is typically disposed of by landfilling or incineration.

Addition of PAC to a biological system does not necessarily involve large capital expenditures for equipment, and may solve many problems. Use of PAC may allow a plant to meet effluent standards and reduce costs. Among the possible benefits are as follows:

- Improved organic pollutant removals [BOD, COD, and total organic carbon (TOC)]
- More uniform operation and effluent quality, particularly during periods of widely varying organic and hydraulic loads
- Adsorption of organics, such as detergents, oils, and dyes that are refractory and nonbiodegradable
- Protection of the biological system from toxic waste components
- More effective removal of organically bound phosphorus and nitrogen
- Increased effective plant capacity at little or no additional capital investment
- Savings on operating costs resulting from reduced defoamer, coagulant, and power requirements
- Greater treatment flexibility since carbon dosages can be varied to match waste strengths and flow rates
- Increased solids retention times in biological processes

Many pollutants, not otherwise biologically degraded, may be removed when adsorbed by carbon added to the mixed liquor. Contact time is extended from hours to days, and pollutants are adsorbed by carbon thoroughly intermixed with biological solids.

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CHAPTER 25

Heavy Metal Removal

Metals are among the oldest known toxins to humans. Lead and arsenic have been recognized for many years as agents responsible for illnesses and death in people. Metals differ from organic toxins inasmuch as they cannot be created nor destroyed. Further, a heavy metal may have a half-life in a human organ of several years. This means that it can take years for the body to cleanse itself of one half of any toxic metals that enter. Because of this long residence time, metals are said to bioaccumulate when introduced into a target organism.

The biochemical mechanism responsible for metal toxicity differs with the metal and the type of organism it enters. The most commonly held mechanism for toxicity involves the bonding of metals to biomolecules in a manner that alters the normal function of the biomolecule. For example, many enzymes require a metal ion to activate catalytic activity. However, it is possible to inhibit normal activity of enzymes through bonding of a foreign metal to the enzyme. This disrupts normal metabolism, resulting in an alteration in the normal life functions of the organism.

Metals are present in the earth's landmass and are naturally introduced to the groundwater and surface waterways at low concentration. Some metals are essential for life when present in trace amounts, but act as toxins if present in higher amounts.

In some facilities, industrial processes produce effluent that is high in the concentration of heavy metals. In order to ensure that aquatic life and food sources are protected from exposure to toxic levels of metals, removal of various metals from effluent to meet safe standards is necessary.

Regulatory Issues

Many industrial countries have implemented regulations on the discharge of pollutants into the environment. Chemicals that have been proven or are suspected as being toxic to the environment are regulated.

Local laws generally specify discharge limits for heavy metals. A daily maximum level or a maximum monthly average may regulate a given metal. Allowable discharge limits are established by an environmental agency based upon impact of the metal on the environment. Metals such as mercury, arsenic, and more recently selenium that carry serious environmental impact, generally receive low discharge limits (in the µg/L range), while other less toxic metals such as iron and nickel, usually have maximum allowable limits in the mg/L range.

Most local regulatory agencies have separate guidelines for direct dischargers and those that send effluent to a public treatment plant. Discharge to a sewer (indirect discharge) is subject to further treatment before water enters the environment, and limits tend to be less severe than for discharge directly to a waterway.

Sources of Metals

Metals are the raw materials used in many industrial processes, and they may concentrate in water through water reuse. Because of the inherent nature of these processes, metals are introduced into effluent from normal operations. Some examples of industrial sources of heavy metals are as follows:

- Spent baths from plating and etching operations
- Rinse water from plating baths
- Air scrubbers from refineries
- Ore process waters
- Waters from casting operations
- Dissolution of metal-containing catalysts

Metals occurring in waste streams, which are listed as hazardous and likely to be subject to discharge limits, are shown in Table 25.1.

Antimony	Chromium	Nickel
Arsenic	Cobalt	Silver
Barium	Copper	Selenium
Beryllium	Lead	Vanadium
Cadmium	Mercury	Zinc

Table 25.1 Common Hazardous Metals in Waste Streams

Chemistry of Metals

Many heavy metals of interest are members of a group known as transition metals. The first series of transition metals are common targets for removal from effluent. This series consists of scandium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, and zinc. Metals such as these are often utilized in industry because they exhibit properties that make them desirable in a variety of applications. In their elemental state, they are hard, strong, high melting, conduct heat and electricity, and in some cases show low corrosion rates.

Metal ions are always surrounded by groups of atoms or molecules that stabilize the ion when it is in a dissolved state. Surrounding groups are referred to as ligands, while the metal ion along with its surrounding groups is referred to as a complex ion or simply a metal complex. Most heavy metals form complexes in solution as a means of forming the most stable configuration for the metallic ion. Ligands can be very simple single atomic species such as chloride (Cl^-) or fluoride (F^-) or more complex ions such as cyanide (CN^-). Neutral molecules like ammonia (NH_3) or water (H_2O) may act as ligands, giving rise to complexes such as $Cu(H_2O)_4^{+2}$ and $Cu(NH_3)_4^{+2}$. A metal always seeks the most stable molecular arrangement.

Ligands may also be organic molecules such as an amine or carboxylic acid. Examples of an amine and carboxylic acid that can complex with a metal are ethanolamine and acetic acid, respectively.

First row transition metals are characterized by bond formation that typically involves the 3d orbital on the metal atom. Ligands are able to donate or share electrons with the metal in the complex.

The 3d orbitals that participate in metal-ligand bonding are spatially arranged in such a manner as to most commonly give rise to octahedral or tetrahedral complex geometries. The most stable configurations are to have the electronic orbital empty, half filled, or completely filled. This is one of the reasons why aluminum (Al^{+3}) does not form precipitate complexes with ethylenediaminetetraacetic acid (EDTA), carbamate, and other chelating agents. The structure of an octahedral and tetrahedral complex for a metal (M) with ligand (L) is shown in Fig. 25.1.

Metals may be coordinated with a number of anions and neutral molecules. This number is called the coordination number of the metal in the complex. The most common coordination numbers for transition metals are four and six. Molecules of these coordination numbers often show the tetrahedral and octahedral geometries shown in Fig. 25.1. Examples of complexes with a coordination number of four include $Zn(CN)_4^{-2}$, $FeCl_4^-$, and $CoBr_4^{-2}$, while examples of complexes with a coordination number of six are $Co(NH_3)_6^{+2}$ and $Cu(NH_3)_5 \cdot H_2O^{+2}$.

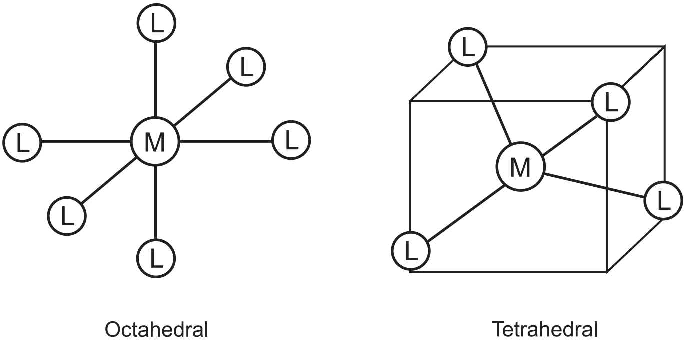


FIGURE 25.1 Tetrahedral and octahedral metal–ligand complexes.

The most common chemical means for removal of a metal ion from effluent is through reaction with a precipitating agent to form an insoluble complex or precipitate. Various precipitation agents used for metal removal in industrial effluent treatment are discussed under Chemical Methods later in this chapter. Equation (25.1) shows the reaction of ferric ion with hydroxide to form insoluble ferric hydroxide.

$$Fe^{+3} + 3OH^- \rightleftharpoons Fe(OH)_3 \tag{25.1}$$

This precipitation is shown as an equilibrium reaction indicating that if ferric hydroxide is added to water, some of the solid dissolves, resulting in a mixture of solid ferric hydroxide, ferric ion, and hydroxide ion. Likewise, if caustic is added to a solution of ferric ion, the same mixture results.

An equilibrium constant can be written for any chemical reaction as a ratio of the concentrations of products divided by the concentrations of reactants after equilibrium is reached. For dissolution of ferric hydroxide [reverse of Eq. (25.1)], the products are Fe^{+3} and OH^-, and the equilibrium constant (K_{eq}) can be expressed as the ratio shown in Eq. (25.2).

$$K_{eq} = [Fe^{+3}][OH^-]^3/[Fe(OH)_3] \tag{25.2}$$

Concentrations need to be raised to the appropriate power as Eq. (25.2) shows for the $[OH^-]$ raised to the power 3. The larger the equilibrium constant for a reaction, the more the reaction favors formation of the products in the reaction as written.

In dissolving ferric hydroxide in water, the concentration of solid ferric hydroxide does not change significantly, and it remains a constant that can be combined with K_{eq} to define the solubility product (K_{sp}).

$$K_{sp} = [Fe^{+3}][OH^-]^3 \tag{25.3}$$

Compound	Chemical Formula	K_{sp} at Room Temperature
Copper (II) carbonate	$CuCO_3$	10^{-10}
Copper (II) hydroxide	$Cu(OH)_2$	10^{-20}
Copper (II) sulfide	CuS	10^{-36}
Lead (II) carbonate	$PbCO_3$	10^{-13}
Lead (II) hydroxide	$Pb(OH)_2$	10^{-15}
Lead (II) sulfide	PbS	10^{-26}
Manganese (II) carbonate	$MnCO_3$	10^{-11}
Manganese (II) hydroxide	$Mn(OH)_2$	10^{-13}
Manganese (II) sulfide	MnS	10^{-13}
Mercury (II) sulfide	HgS	10^{-50}
Nickel (II) carbonate	$NiCO_3$	10^{-9}
Nickel (II) hydroxide	$Ni(OH)_2$	10^{-15}
Nickel (II) sulfide	NiS	10^{-22}
Zinc (II) carbonate	$ZnCO_3$	10^{-11}
Zinc (II) hydroxide	$Zn(OH)_2$	10^{-17}
Zinc (II) sulfide	ZnS	10^{-24}

TABLE 25.2 Solubility Products for Various Metal Salts in Pure Water

K_{sp}, as defined in Eq. (25.3), is the solubility product for ferric hydroxide in water. Since temperature affects solubility of all solids, the value of K_{sp} is reported for a specific temperature. The solubility product is a measure of the tendency of metals to precipitate when the appropriate anion is added to a solution of the metal. In general, the smaller the solubility product (K_{sp}), the less soluble the compound and the more effectively a metal can be removed from solution. Ferric hydroxide is among the least soluble metal hydroxides (MOHs) ($K_{sp} = 1.1 \cdot 10^{-36}$), and ferric ion is very effectively removed from solution by addition of caustic.

Table 25.2 shows solubility products for some common MOHs, carbonates, and sulfides in pure water. Their low K_{sp} makes hydroxide, sulfide, and carbonate effective precipitation agents for metal removal.

Ionic Strength

Solubility of a precipitate is affected by ionic strength of the medium in which it dissolves. Ionic strength is simply a measure of all dissolved ions in solution and is therefore related to conductivity of the water. Waste streams often have numerous dissolved salts that

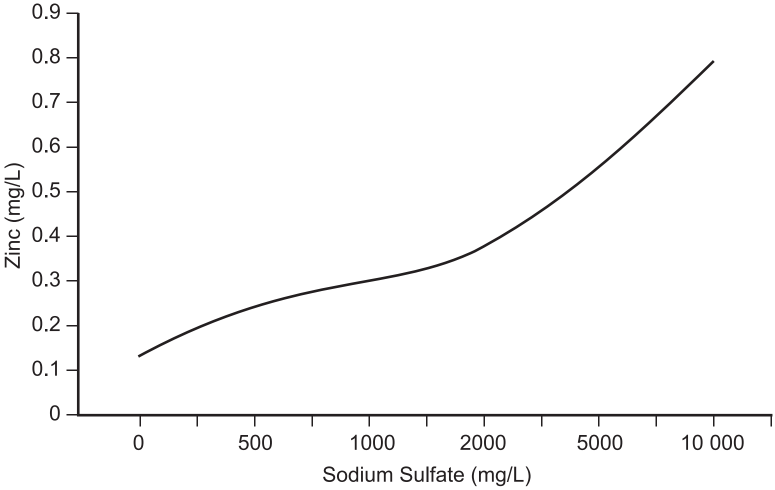


Figure 25.2 Effect of sodium sulfate on solubility of zinc hydroxide.

produce water with significantly higher ionic strength than that of pure water. Though the solubility products given in Table 25.2 offer a measure of the effectiveness of a precipitation agent, added ionic strength can offer enhanced solubility for precipitates.

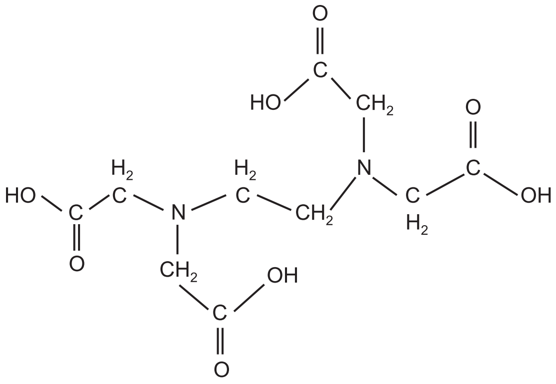
The reason for this greater solubility lies in the attraction that precipitate ions have for other ions in solution. In general, high ionic strength (high conductivity) solutions can enhance solubility of a precipitate by two to threefold over that observed for pure water. Figure 25.2 shows the effect of a dissolved salt (sodium sulfate) on the solubility of zinc at pH 9.2. Salts other than sodium sulfate show similar effects.

Since ionic effects are determined by interactions between charged species, higher valence ions generally show greater solubility increases than is seen for monovalent metal salts.

One of the unfortunate consequences of employing recycling practices in a plant is to produce a process water with higher dissolved salts that reduces performance of precipitation processes.

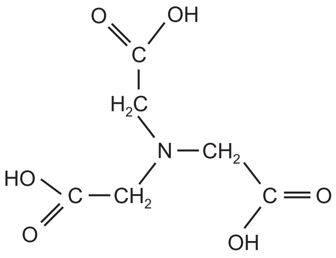
Chelation Effects

Chelating agents or chelants are ligands that possess two or more donor groups capable of simultaneously bonding to a metal. Chelating agents are often found in industrial products such as cleaners and therefore make their way into effluent. Examples of two of the most common chelating agents, EDTA and nitrilotriacetic acid (NTA), are shown in Figs. 25.3 and 25.4. Figure 25.5 shows the structure of the octahedral complex that is formed when a metal (M) is coordinated



EDTA

Figure 25.3 Chemical structure for EDTA.



NTA

Figure 25.4 Chemical structure for NTA.

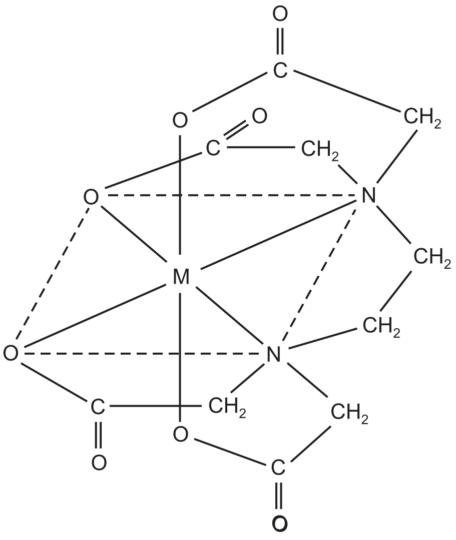


Figure 25.5 Chemical structure for metal–EDTA complex.

with the chelant (EDTA). A general feature of the chelant-metal structure is the formation of five and six member rings that leads to enhanced stability of the metal–chelant complex.

Presence of chelating agents in metal bearing effluent can make removal of metal ions by precipitation much more challenging. Chelated metals are bonded in stable water-soluble complexes that must be disrupted in order to be removed through chemical treatment such as precipitation.

Chelating agents (C) react with metals (M) in a manner that is schematically represented by Eq. (25.4).

$$\mathrm{M} + \mathrm{C} \rightleftharpoons \mathrm{MC} \tag{25.4}$$

The equilibrium constant (called the formation constant K_f) for this reaction is expressed in Eq. (25.5).

$$K_f = [\mathrm{MC}]/[\mathrm{M}][\mathrm{C}] \tag{25.5}$$

In practice, more than one chelant molecule can react with a single metal, resulting in a second equilibrium expression. Formation constants for metal–EDTA complexes are given in Table 25.3.

Chelants present a competing equilibrium problem when a metal is treated with a precipitation agent in a chelant-metal effluent. The metal has an opportunity to complex with the chelant remaining in solution or reacting with the precipitant to form an insoluble salt. This situation can be expressed in the chemical equilibrium reaction shown in Eq. (25.6).

$$\mathrm{MC} + \mathrm{OH} \rightleftharpoons \mathrm{MOH} + \mathrm{C} \tag{25.6}$$

In this reaction, hydroxide ion must compete with chelant (C) for formation of insoluble MOH. The equilibrium constant for this reaction is shown in Eq. (25.7).

$$K_{eq} = [\mathrm{MOH}][C]/[\mathrm{MC}][\mathrm{OH}] \tag{25.7}$$

Metal	K_f
Mn (II)	10^{13}
Co (II)	10^{16}
Ni (II)	10^{18}
Cu (II)	10^{18}
Zn (II)	10^{16}
Cd (II)	10^{16}
Pb (II)	10^{18}
Fe (III)	10^{25}

TABLE 25.3 Formation Constants (K_f) for Various Metal–EDTA Complexes

This equilibrium constant can be written as a ratio of the solubility product (K_{sp}) and the formation constant (K_f) as shown in Eq. (25.8).

$$K_{eq} = (1/K_{sp})(1/K_f) \tag{25.8}$$

Therefore, the solubility product (K_{sp}) for precipitation and the chelant-metal formation constant (K_f) give an idea whether a metal that is chelated can be precipitated with a chemical precipitation agent. The larger the product of the inverse of K_{sp} and K_f, the more likely Eq. (25.6) will favor precipitation. In the reaction of Fe (III)-EDTA with hydroxide, $K_{sp} = 10^{-36}$ while $K_f = 10^{25}$. Therefore, K_{eq} defined in Eq. (25.8) is 10^{11}. In this case, the precipitation reaction wins out over the chelation reaction, and ferric iron can be removed from effluent containing EDTA. For many precipitation reactions, the K_{sp} and K_f product defined in Eq. (25.8) is not as large as this example, indicating that chelants have a strong influence on the ability of precipitation agents to remove metals through formation of a precipitate. An example is EDTA chelated zinc, which does not precipitate with hydroxide or sulfide precipitation chemistries.

Metal Removal

The best approach to heavy metal pollution control is a comprehensive program of prevention practices and point source treatment. This may include production modifications, operational changes, material substitution, materials and water conservation, recycling, and end-of-pipe chemical and equipment treatment. In other words, a successful environmental management system requires a mechanical, operational, and chemical (MOC) approach in order to meet regulatory compliance.

Operational Factors

Several operational factors can contribute to successful environmental management. These include training and supervision, production planning, raw material substitution, waste segregation and separation, loss prevention and housekeeping, and closed loop recycling.

Training and Supervision**—**Training of employees ensures that all are aware of the company goals in meeting regulatory guidelines. It also emphasizes that equipment must be operated as designed in order to minimize waste.

Production Planning**—**Production planning can eliminate unnecessary steps such as cleaning operations that contribute to overall waste generated.

Raw Material Substitution**—**Where possible, toxic raw materials and products should be replaced with less hazardous substitutes. For example, replacement of hexavalent chromium and cyanide in plating and metal finishing operations reduces toxicity of waste generated.

Waste Segregation and Separation**—**Facilities need to develop treatment plans that handle hazardous and nonhazardous waste separately. Mixing wastes complicates removal of hazardous components. For example, cyanide-bearing effluent should be pretreated before mixing with other waste streams.

Loss Prevention and Housekeeping**—**Maintenance of equipment to minimize spills and leaks are a necessary part of an environmental management system. Use of chemical analysis, rather than elapsed time or production numbers, to determine when process solutions need replacement can reduce waste.

Closed Loop Recycling**—**Closed loop recycling is often linked to mechanical or equipment methods in waste treatment. Any equipment treatment process [e.g., ion exchange and reverse osmosis (RO)] that is capable of separating or concentrating metals so that they can be returned to the process is of great value in reducing the amount of metals that are treated in an end-of-pipe treatment. Separation and concentration methods that form a recycle loop are discussed below.

Equipment Methods

Most mechanical options discussed in this section fall into the category of physical separation techniques and are therefore mainly equipment related processes. Most of these processes generate concentrated solutions of the metal, which still may require chemical treatment for disposal or reuse.

Production mechanical changes should be implemented where possible to affect overall success of the pollution control program. Whenever possible, equipment should be evaluated for modifications that minimize the amount of metal-bearing effluent generated. For example, changing the rack configuration in a plating process may be able to reduce drag-out and lower overall metal in effluent.

Ion Exchange

Ion exchange is a reversible chemical reaction where ions in a feed stream are exchanged for similarly charged ions on the surface of a solid ion exchange resin. Ion exchange resins vary widely in composition, but all resins contain charged groups that attract ions of opposite charge. Ion exchange resins are classified as anion or cation, depending upon the type of charged species they exchange. Typically, cation exchange resins exchange hydrogen (H^+) for other cations such as metals. This resin is the most widely used in effluent applications, since removal of cations is a common goal in effluent treatment.

Anion exchange resins often exchange hydroxide (OH^-) for anions in a feed water stream.

Once capacity of the resin is reached (most ions of the resin are exchanged), the resin is taken out of service for regeneration. Cation resins are most often regenerated using a mineral acid, while anion resins are regenerated using caustic. In the regeneration process for cation resin, a concentrated metal-bearing stream is produced that can be recycled, if possible, or further treated for metal removal.

Ion exchange can be used as an in-process treatment for closed loop recycling or an end-of-pipe treatment for removal of toxic ions to meet regulatory compliance.

In treatment facilities where divalent metal ions are targeted for removal, selective resins are sometimes employed. This process is referred to as scavenging. The regeneration process produces a highly concentrated metal containing regenerant that is suitable for recovery of the metal.

Membrane Filtration

Membrane filtration techniques utilize a membrane and a driving force to separate dissolved species and finely divided particles from liquids. The most common membrane filtration methods used in treatment of effluent are electrodialysis (ED), microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and RO. A comparison of these techniques is shown in Table 25.4. Figure 25.6 shows separation characteristics for these processes.

Membrane Process	Driving Force	Membrane Type	Size Limit	Application
ED	Electric field gradient	Anion and cation specific	Dissolved ions	Electroplating waste streams
MF	Pressure gradient	Ceramic and polymeric	0.1–10 μm particles	Removal of suspended solids and oil/water
UF	Pressure gradient	Ceramic and polymeric	10–100 nm	Removal of colloidal material, dissolved oils, bacteria, high MW organics
NF	Pressure gradient	Polymeric	1–10 nm	Removal of dissolved salts
RO	Pressure gradient	Polymeric	<1 nm	Removal of dissolved salts

Table 25.4 Comparison of Membrane Filtration Methods

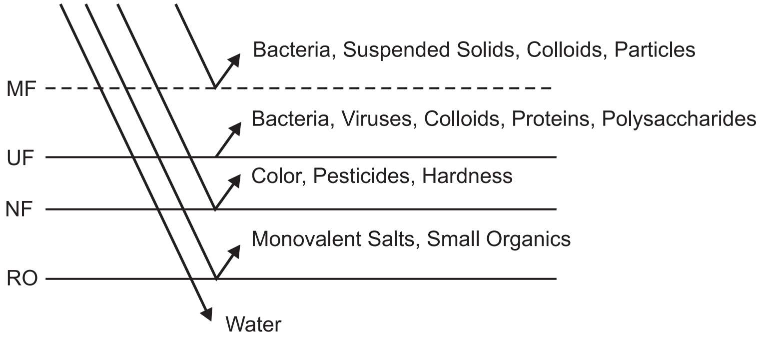


Figure 25.6 Separation characteristics of MF, UF, NF, and RO processes.

Electrodialysis ED uses a set of anion and cation specific membranes to form a set of compartments. A static electric field is applied across the membrane assembly to generate an electric field gradient. The unit consists of a membrane stack and a rectifier, which converts alternating current (AC) to direct current (DC), so that a static electric field can be applied.

The waste stream enters parallel to the membrane stack perpendicular to the field direction. Anions and cations are attracted to the anode and cathode, respectively. The ion selective membranes are semipermeable. The cathode transport membrane allows passage of only cations migrating toward the cathode, while the anion transport membrane allows anions to pass toward the anode. Ions pass to an adjacent compartment before becoming trapped by an opposing type of membrane that does not allow passage. The net result is the production of a series of alternating concentrated and depleted ionic compartments (see Fig. 25.7). Facilities typically use ED to remove metal ions from electroplating effluent.

Microfiltration, Ultrafiltration, and Nanofiltration MF, UF, and NF all separate particulate, colloidal, or dissolved species by passage of solute through a membrane. All of these methods rely on separation based on the size and shape of the particulate or solvent species. The major difference between MF, UF, and NF lies in the membrane construction and resulting pore size of the membrane used. This dictates the effective size separation range of the various filtration methods (see Fig. 25.8).

Table 25.4 shows the effective separation range associated with MF units. Separation limits of the MF process (0.1–10 μm) make it most useful in separation of finely dispersed particulate or in separation of oil from water. In heavy metal removal, MF may be used in conjunction with various precipitation techniques to reach low levels of metals in treated effluent. In cases where soluble metals are reduced

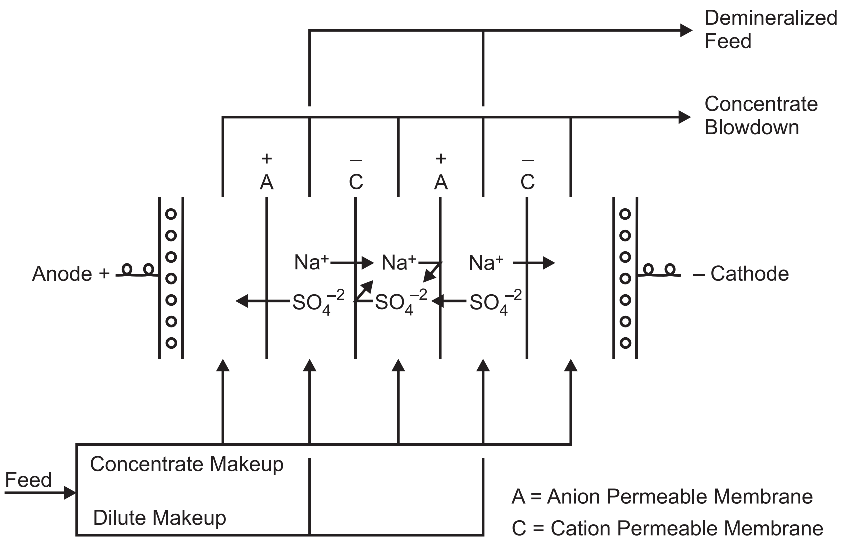


Figure 25.7 ED process.

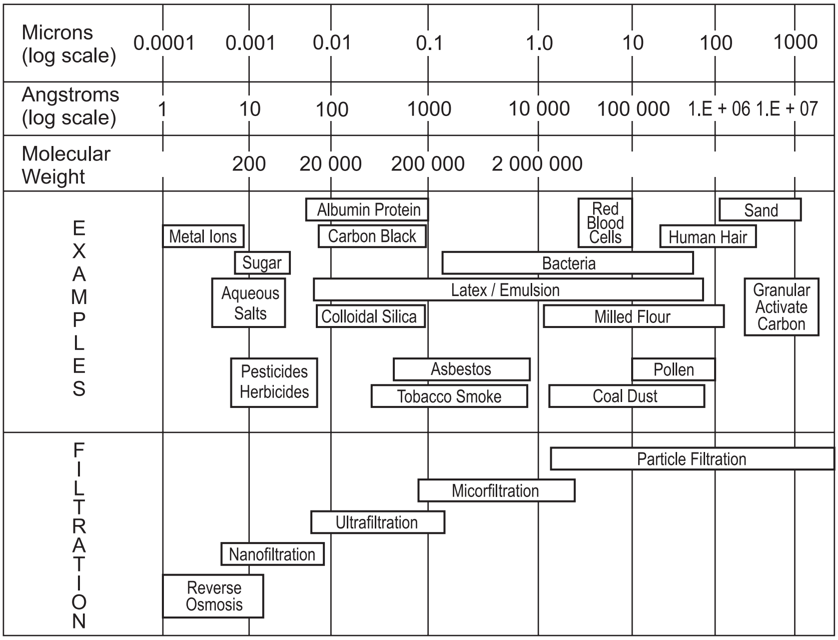


Figure 25.8 Filtration methods and particle size relationships.

below the discharge target range, achieving the discharge target becomes a solid–liquid separation issue. Gravity clarifiers may not produce effluent where total heavy metal (soluble plus particulate) meets discharge limits. In these cases, removal of finely dispersed metal precipitate with MF should be considered.

Reverse Osmosis RO is the most widely used membrane filtration process in treatment of waste and raw water. Osmosis is the tendency of a liquid to pass spontaneously from a dilute to a concentrated salt solution, when the solutions are joined by a semipermeable membrane. If pressure greater than the osmotic pressure is applied to the concentrated solution, liquid (and some small ions) passes through the membrane to the dilute liquid. This pressure driven osmosis process is termed RO. It is easily seen that this process is capable of producing a concentrated dissolved salt stream and a clean stream when effluent is fed to an RO unit.

Table 25.4 shows the working range of size separation that can be achieved with RO membranes. The effective size range for RO makes the technique applicable for removal of atomic sized species. In fact, RO has the capability of retaining 99% of multivalent ions and about 95% of monovalent ions in the concentrated (reject) stream.

RO membranes are constructed of organic materials and may be configured in a variety of designs, similar to designs used in other membrane filtration processes. Operating pressures are significantly higher in RO than other membrane filtration systems and range from 400 to 1000 psig (2.8–6.9 MPag). Capacity of an RO unit is determined by operating pressure and surface area of the membrane. Higher operating pressure and surface area generally increase throughput volume (flux). Reject stream concentration increases with pressure and decreases with flow volume (effective residence time). The maximum achievable concentration in a reject stream is usually between 20 and 30 g/L of total dissolved solids (TDS). Refer to Chap. 8 for more information on RO systems.

This technique is most applicable for concentrating a heavy metal for recycling, or coupling with other methods such as electrolytic recovery or evaporation to recover the metal. RO has been used effectively in electroplating rinse waters. If the reject stream is acceptable for return to the plating bath, a closed loop can be created where permeate is also returned to a rinse bath. Often, however, reject stream concentration is not suitable for recycling, and metals must be further treated for removal.

RO has higher capital costs than ion exchange, if both processes are coupled with electrolytic recovery. Both methods are equally effective in removal of heavy metals, but RO can handle higher feed stream concentrations. Both methods produce about the same concentration factors in the reject and regenerant streams.

For most operations, membrane life is usually five years, if proper precautions and maintenance are observed. Flux rates should be monitored as a means of determining when membrane cleaning is needed.

Electrolytic Recovery

Electrolytic recovery is an electrochemical process for removal of metals from a waste stream. A metal-bearing solution is processed in an electrolytic cell that consists of a pair of closely spaced electrodes that receive an applied potential. Current is applied across the cell, and metal ions are reduced to their elemental state at the cathode of the cell. The overall unit is made up of one or more cells, a transfer pump, and a rectifier to supply the potential.

Capacity of the equipment depends on total surface area of the cathode, with surface areas that range from 1 to 10 ft^2 (0.09–0.9 m^2). The reduction process is governed by Faraday's Law, which states that the amount of chemical reduction (recovery) is proportional to the electric current applied. Flat electrodes are used to recover metals from solutions that contain 1 to 20 g/L of dissolved metal. Reticulate cathodes having a woven fiber design possess significantly higher surface area than flat electrodes and are used for metal recovery from solutions containing less than 100 mg/L dissolved metal.

Chemical Methods

Chemical methods of metal removal are often the most cost-effective processes to meet regulatory discharge limits. However, as discharge limits are lowered, chemical removal methods likely need to be coupled with other techniques to produce effluent that satisfies government regulations. In general, chemical precipitation works best on more concentrated metal solutions. Low concentration solutions (50–250 μg/L) are very difficult to treat, as contact between the metal and precipitating chemical is greatly reduced. To overcome this issue, higher dosages of precipitating chemical are used, and if not very accurately controlled, can lead to redispersion of metal precipitate.

The most widely used end-of-pipe treatment for removal of heavy metals is chemical precipitation and flocculation followed, by separation of resulting floc. When properly monitored and controlled, chemical precipitation is a very effective means of metal removal in many waste streams. It currently is by far the most cost-effective means of reducing metal concentration to meet local environmental regulations. Several agents are used to form insoluble salts with heavy metals. The most common precipitants are hydroxide, sulfide, carbonate, small organic molecules, natural molecules, iron hydroxide (iron co-precipitation), and synthetic polymers.

The rate at which precipitate forms is an important practical consideration in removal of metal ions through precipitation techniques. Unfortunately, no conclusions can be reached about the rate that precipitate forms from the magnitude of the solubility product. Some precipitates with very small K_{sp} proceed to equilibrium at very slow rates. Precipitates can be slow to form, requiring contact times of minutes or even hours. This may complicate removal by limiting throughput in a treatment plant.

Hydroxide Precipitation

Hydroxide precipitation is the most common chemical method of heavy metal removal. Reaction of a divalent metal with sodium hydroxide to form the MOH is shown in Eq. (25.9).

$$M^{+2} + 2NaOH \rightleftharpoons M(OH)_2 + 2Na^+ \tag{25.9}$$

Table 25.2 shows that some MOHs have limited solubility (small K_{sp}) in water, making this method very effective in removing metals from solution. Figure 25.9 shows metal solubility as related to pH through the precipitation reaction shown in Eq. (25.9).

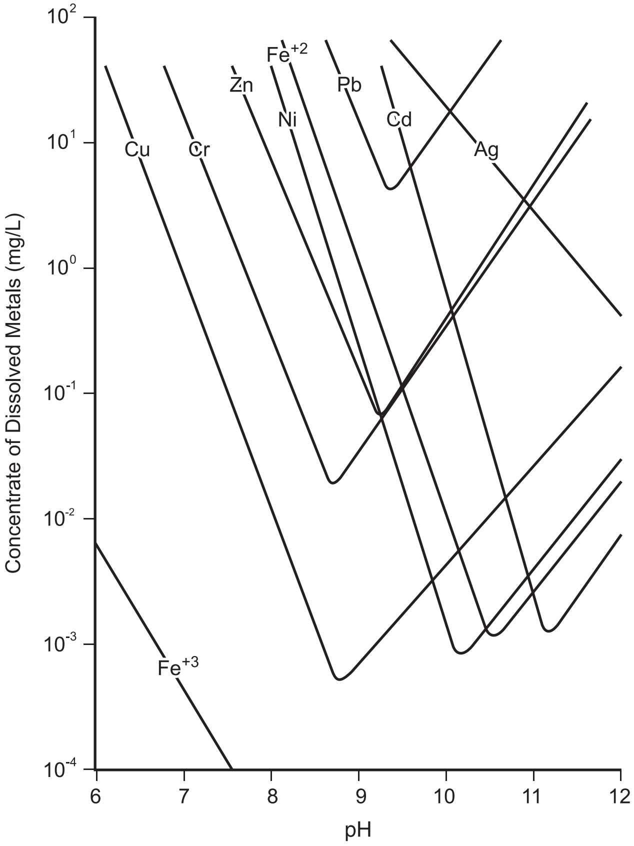


Figure 25.9 Solubility of various metals versus pH.

By examining the solubility curves in Fig. 25.9, we can make two important observations. MOHs of several heavy metals have very small solubility products, (K_{sp}), and the equilibrium reaction shown in Eq. (25.9) greatly favors the insoluble hydroxide. Secondly, solubility is influenced by pH, suggesting that MOHs, in some cases, form complexes with excess hydroxide with increased solubility. Equation (25.10) shows the reaction of zinc hydroxide with excess caustic to form the more soluble zincate ion [$Zn(OH)_3^-$]. Just as chelants interfere with precipitation equilibrium, the reaction shown in Eq. (25.10) presents another competing process.

$$Zn(OH)_2 + OH^- \rightleftharpoons Zn(OH)_3^- \qquad (25.10)$$

This type of chemistry is observed for several heavy metals shown in Fig. 25.9 and indicates that proper pH control is critical in removal of these metals from solution.

Metals that can be effectively removed through hydroxide precipitation include arsenic, cadmium, chromium III, copper, iron, manganese, nickel, lead, and zinc.

For economic reasons, the preferred reagent used to furnish hydroxide ion for precipitation is quick lime (CaO) or hydrated lime [$Ca(OH)_2$]. Other precipitants such as sodium hydroxide (NaOH) and magnesium hydroxide [$Mg(OH)_2$] are also used. Though lime is often used, it is more difficult to control addition of a solid or slurry than feed of a liquid such as sodium hydroxide. In addition to application benefits with sodium hydroxide, sodium salts are generally very soluble, and unlike lime, caustic does not produce as much sludge due to insoluble by-products.

Hydroxide precipitation offers the most cost-effective method of heavy metal removal. It can produce, in many cases, effluent that meets regulatory discharge requirements for the metal. However, there are problems associated with this technique that may make it difficult to apply as a sole treatment scheme.

- In mixed metal wastes, it may be difficult to find a single pH that is effective for precipitation of all regulated metals. Multiple precipitation steps at different pH may be effective but in practice can be impractical.
- Hydroxide precipitation can be ineffective, if effluents contain chelants or complexing agents.
- In systems that process large volumes of water, this technique may be impractical.
- Sludge that is produced can be voluminous and difficult to filter, resulting in high handling costs.

Sulfide Precipitation

This process is similar to hydroxide precipitation; inasmuch as soluble metal is reacted with a reagent (sulfide) to form an insoluble metal sulfide complex. Equation (25.11) shows the reaction of a divalent metal ion (M^{+2}) with sulfide ion (S^{-2}) to form insoluble metal sulfide (MS).

$$M^{+2} + S^{-2} \rightleftharpoons MS \tag{25.11}$$

Sulfide precipitation is often a more effective alternative to hydroxide, since metal sulfides generally have lower solubility and much higher binding constants. Thus, sulfides can displace chelants better than hydroxides and force reaction toward the insoluble precipitate. Very low levels of metals can be achieved with sulfide precipitation compared to corresponding hydroxide precipitation. Copper, cadmium, zinc, and mercury can be effectively precipitated with short contact time.

Sulfide precipitation uses either soluble sulfide or insoluble sulfide as the source of the sulfide reagent. In soluble sulfide precipitation (SSP), water soluble sulfides such as hydrogen sulfide (H_2S), sodium sulfide (Na_2S), or sodium hydrogen sulfide (NaHS) serve as the source of sulfide. In insoluble sulfide precipitation (ISP), insoluble sulfide salts [e.g., ferrous sulfide (FeS)] are used.

Sulfide precipitation has both advantages and disadvantages compared to hydroxide precipitation. Advantages include:

- Lower residual dissolved metal concentration is achieved, since sulfides are less soluble than hydroxides.
- Sulfide can be effective in precipitating metal even in the presence of chelating agents.
- Sludge is less subject to leaching than hydroxide sludge.
- Sludge tends to be easier to filter and dewater.
- Dichromate and chromate can be removed without reduction to the trivalent state.
- Mixed metal streams can be treated at the same pH.
- Disadvantages associated with sulfide precipitation include:
- Higher cost compared to hydroxide.
- Potential for generation of H_2S gas (highly toxic) if contact is made with acidic effluent.
- Residual sulfide ion is toxic, and care must be taken to insure its discharge limit is not exceeded.
- Optimization of the solid–liquid separation with coagulation and flocculation can be difficult.

Carbonate Precipitation

Carbonate precipitation uses addition of carbonate ion (CO_3^{-2}) to effluent to remove metals as insoluble metal carbonates. The reaction of a divalent metal (M^{+2}) with carbonate ion to form an insoluble carbonate salt is shown in Eq. (25.12).

$$M^{+2} + CO_3^{-2} \rightleftharpoons MCO_3 \qquad (25.12)$$

Solubility of metal carbonate salts generally falls between MOHs and metal sulfides, though some metals are not removed effectively in a carbonate precipitation process. Metals such as cadmium can be effectively removed at neutral pH, if sufficient carbonate is available to drive the reaction shown in Eq. (25.12). Lead can be removed more efficiently with carbonate than hydroxide, since lead carbonate lends itself to easier filtration.

Sodium carbonate, calcium carbonate, and carbon dioxide are all used as carbonate sources. When introduced into water, carbon dioxide dissolves to form carbonic acid, which upon pH adjustment forms carbonate.

Advantages that carbonate precipitation can provide over other methods include:

- Process for specific metals (cadmium and lead) is more effective than hydroxide precipitation.
- Metal carbonates are denser than hydroxides, offering easier separation.
- Disadvantages encountered with carbonate precipitation systems are as follows:
- Higher cost than hydroxide systems.
- Long retention times necessary (greater than 45 minutes).
- Release of carbon dioxide can result in foaming and floating sludge.

Small Organic Molecule Precipitation

Small organic molecule precipitants are low molecular weight (less than 500) organic sulfides that have strong affinity for metals. Figure 25.10 shows the chemical structure for dimethyldithiocarbamate (DTC), trithiocarbamate (TTC), and trimercaptotriazine (TMT), three of the more commonly used organic precipitants.

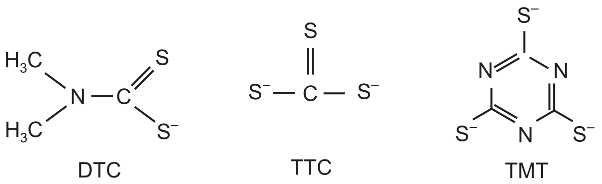


FIGURE 25.10 Chemical structure for common organic sulfide precipitants.

Molecules of this type react with metals in a stoichiometric manner to form complexes that, like inorganic sulfides, have limited water solubility. Equation (25.13) shows the reaction of DTC with a divalent metal to illustrate stoichiometry of the reaction. Two moles of DTC are required to precipitate each mole of divalent metal (M^{+2}).

$$2DTC^{-} + M^{+2} \rightleftharpoons M(DTC)_2 \qquad (25.13)$$

Advantages of organic precipitants are as follows:

- DTC is a very effective precipitant, and low residual metal can be achieved.
- Moderate cost for DTC.
- TMT is nontoxic.
- Disadvantages are as follows:
- DTC has very high aquatic toxicity.
- TMT is relatively high cost.
- All require coagulation and flocculation.
- Optimization of precipitation and solid–liquid separation can be difficult.
- Overfeed leads to high cost and effluent toxicity.

Iron Hydroxide (Iron Co-precipitation)

Iron co-precipitation is a common variation of the hydroxide precipitation process. It is very effective at reducing the concentration of metals such as arsenic, beryllium, cadmium, copper, lead, nickel, and zinc to levels below that achieved with hydroxide precipitation. Iron co-precipitation involves adding an iron source (ferric sulfate or ferric chloride) to effluent at the pH adjustment stage. As pH increases, iron hydroxide precipitates along with the target heavy metals. The target metals may be incorporated as impurities into the iron hydroxide matrix or physically entrapped within iron hydroxide precipitate. MOHs can also be adsorbed onto the surface of iron hydroxide precipitate.

Factors that affect effectiveness of this technique include iron dosage, pH, initial concentration of target metals, and competition for adsorption sites from other species. The process requires some effort to optimize.

Synthetic Polymer Precipitation

A synthetic polymer has been developed that reacts with metals to form insoluble complexes. A schematic structure of this polymer is shown in Fig. 25.11.

This polymer incorporates the metal binding structural feature into a polymer structure. The main advantage of the polymeric

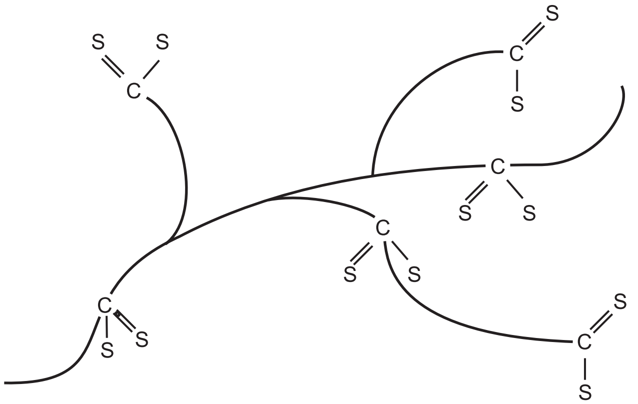


FIGURE 25.11 Chemical picture of synthetic polymer precipitant.

sulfide is that simultaneous precipitation and clarification take place in a single step. This means that good solid–liquid separation can be achieved without optimization of a second chemical.

A second important advantage with the polymeric precipitant is reduced aquatic toxicity compared to small organic sulfides. This factor becomes important in a situation where precipitant is overdosed or where there is concern for chemical toxicity on secondary biological systems.

Monovalent ions form stronger complexes with this polymer than divalent ions. Metals are therefore removed from the system in the order:

$$Hg > Ag > Cd > Cu > Pb > Zn > Co > Ni > Fe > Mn$$

The polymer works best at neutral pH, though zinc removal is more effective at lower pH. At elevated pH, it is possible to benefit from hydroxide precipitation and polymer co-precipitation.

Metallic Replacement/Cementation

Metallic replacement or cementation is a process in which dissolved metal ions are spontaneously displaced from solution by another metal. An example of this process is shown in Eq. (25.14) where dissolved copper is replaced by iron.

$$Cu^{+2} + Fe^{0} \rightarrow Cu^{0} + Fe^{+2} \tag{25.14}$$

This type of reaction does not proceed spontaneously for all pairs of metals, and this process has limited application. It has its widest application for recovery of copper, but it can be applied to recovery of silver paired with iron metal and mercury paired with iron or zinc metal.

The main advantage of the method is that it utilizes scrap metal to recover a higher value metal. In addition, no energy costs are involved in the recovery.

The main disadvantage is that the target metal [copper in Eq. (25.14)] is replaced by another metal (iron) that needs to be removed from the waste stream.

Chemical Reduction

In any reduction reaction, electrons flow from the reducing agent to the species that is reduced. In the removal of metal ions from solution, reducing agents such as sodium borohydride, hydrazine, and sodium bisulfite furnish electrons to the metal ions. Upon reduction, the metal in its neutral metallic state forms an insoluble precipitate that can be removed through standard separation methods.

Ionic mercury can be effectively converted to metallic form through use of reducing agents such as hydrazine, stannous chloride, and sodium borohydride.

Chemical reduction works well even when metals are chelated with agents that make chemical precipitation difficult. This characteristic is one of the main advantages with all electrolytic and chemical reduction processes.

Associated Pretreatment

There are varieties of effluent compositions that require pretreatment or special processing before implementation of metal removal techniques.

Chromium Reduction

Chromium is commonly found in effluent from processes such as anodizing, conversion coating, and electroplating. Hexavalent chromium poses significant environmental concerns due to its toxicity to humans. This toxicity has prompted its removal as a corrosion inhibitor in applications such as open cooling water systems. However, despite its toxicity, it remains popular in the plating industry due to the corrosion resistant nature and brightness of chromium surfaces.

Hexavalent chromium (Cr^{+6}) exists in aqueous solution as the chromate ion (CrO_4^{-2}) and does not form insoluble precipitate with hydroxide. Therefore, in order to precipitate chromium as chromium hydroxide, Cr^{+6} must first be reduced to trivalent chromium (Cr^{+3}). Reduction simply means that electrons flow to the hexavalent chromium, and the valence state is reduced from plus 6 to plus 3. Electrons in a reduction reaction can be supplied through an electrode (cathode) as in electrolytic reduction, or can be furnished chemically through a compound that is termed a reducing agent. Chemical reduction is the industrial process used in the reduction of chromium. Sodium metabisulfite, sodium bisulfite, and sulfur dioxide are the most commonly used reducing agents in industrial chromium pretreatment. In practice, the solution must be reduced to pH 2 for the chemical reduction to proceed at a significant rate. At pH levels above 5, the reduction rate is slow, and oxidizing agents such as dissolved oxygen and ferric ion consume the reducing agent. Equation (25.15) shows the reaction of chromate (chromic acid) with sulfur dioxide.

$$2H_2CrO_4 + 3SO_2 \rightarrow Cr(SO_4)_3 + 2H_2O \qquad (25.15)$$

Figure 25.12 shows a typical chrome treatment system. Pretreatment takes place in the initial tank where pH is adjusted to approximately 2 followed by addition of a chemical reducing agent. Addition of reductant is controlled by a probe that measures oxidation–reduction potential (ORP), so that the proper stoichiometric amount is added. Typical reaction time is 15 to 45 minutes for this pretreatment step. After conversion of hexavalent chromium to trivalent chromium has been accomplished, precipitation, and removal of the insoluble hydroxide takes place in the neutralization and settling tanks. Equation (25.16) shows the neutralization step that results in formation of insoluble chromium hydroxide [$Cr(OH)_3$].

$$Cr_2(SO_4)_3 + 6NaOH \rightarrow 3Na_2SO_4 + 2Cr(OH)_3 \qquad (25.16)$$

The pH is adjusted to 7.5 to 8.5, which is effective in precipitation of Cr^{+3} and meets pH discharge limits. The graph in Fig. 25.9 shows that Cr^{+3} solubility reaches a minimum at about pH 8.5.

The process can be semi-automated, so that a pH controller and ORP probe control pH adjustments and reducing agent addition. Though ORP is sensitive in the control of reducing agent to ensure

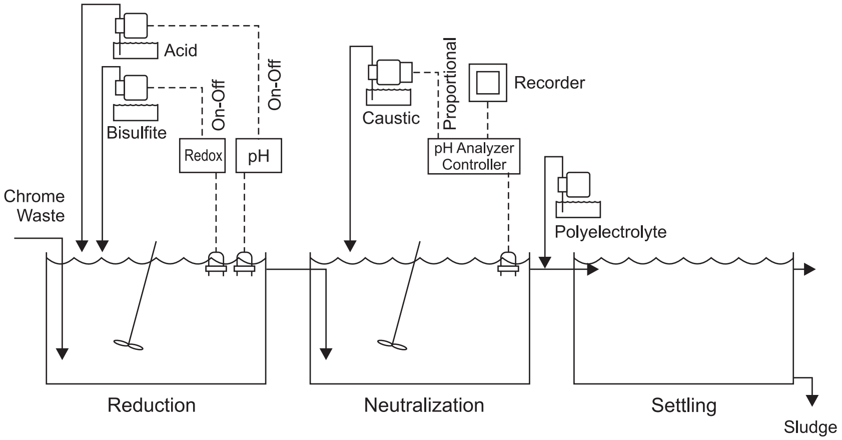


Figure 25.12 Typical chromium treatment system.

that a sufficient amount of reductant is added, analytical testing needs to be done to determine chromium levels in the treated water accurately.

Cyanide

Cyanide (CN^-) solutions are used in plating processes for zinc, cadmium, copper, brass, silver, and gold. In addition to its toxicity, cyanide forms soluble complexes with metals that hinder subsequent removal with precipitation agents. The plating industry is moving toward replacing cyanide with more environmentally friendly agents, but cyanide is still used in many plating operations. In fact, in the United States alone, there are over 1100 plating facilities that have the need to remove cyanide.

Cyanide must be removed from rinse waters in a pretreatment process that typically reduces the level of cyanide below 1 mg/L. The most frequently practiced pretreatment process involves destruction of cyanide in a two-stage alkaline chlorination process. Figure 25.13 shows a typical diagram of a two-stage cyanide treatment system.

In the first stage, pH is adjusted to approximately 11, and chlorine gas or sodium hypochlorite is added to oxidize cyanide to cyanate (CNO^-). Reaction of sodium cyanide with chlorine is shown in Eq. (25.17).

$$Cl_2 + NaCN + 2NaOH \rightarrow NaCNO + 2NaCl + H_2O \qquad (25.17)$$

In the second stage, pH is lowered to 8 to 9, and more oxidant is added to further oxidize cyanate to carbon dioxide and nitrogen. Oxidation of sodium cyanate with chlorine is shown in Eq. (25.18).

$$3Cl_2 + 4NaOH + 2NaCNO \rightarrow 2CO_2 + N_2 + 6NaCl + 2H_2O \qquad (25.18)$$

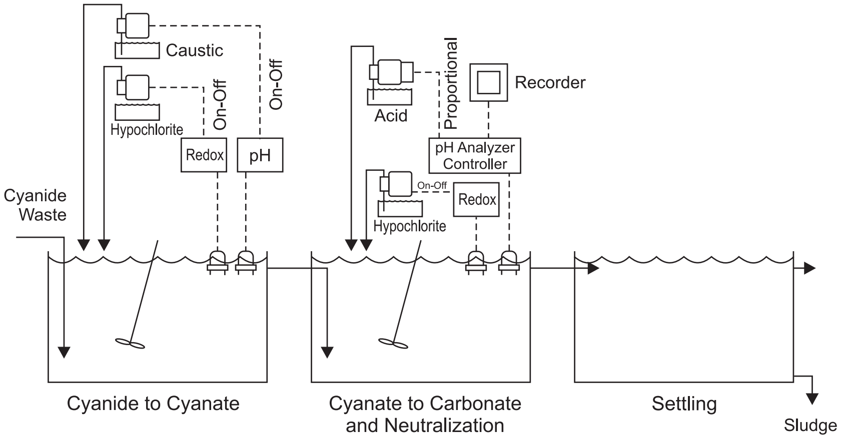


FIGURE 25.13 Typical cyanide treatment system.

The first stage reaction is monitored and controlled by two independent loops. Caustic addition is controlled by a pH controller, which is set to deliver caustic when the pH is below set point. Chlorine addition is controlled with an ORP probe that calls for oxidant to maintain a specified ORP in the tank.

In the second stage, pH is lowered to about 8.5 through addition of sulfuric acid. This pH promotes the second oxidation reaction and produces effluent with a pH suitable for discharge. Acid addition must be done with care so that pH does not fall below 7, since that promotes formation of highly toxic hydrogen cyanide fumes. Chlorine addition is controlled by ORP or is added in proportion to the addition in the first stage.

A final step in pretreatment involves use of a settling tank, clarifier, or filter to remove suspended MOHs that may have precipitated. Further treatment may be necessary to reduce metal concentrations to a level below the discharge limit.

A less common treatment method for cyanide destruction involves oxidation by ozone (O_3). Ozone is a powerful oxidizing agent but must be generated on-site and delivered directly to the treatment tank. Equations 25.19 and 25.20 show the two-step oxidation of cyanide by ozone.

$$\mathrm{CN^- + O_3 \rightarrow CNO^- + O_2} \tag{25.19}$$

$$\mathrm{2CNO^- + 3O_3 + H_2O \rightarrow 2HCO_3^- + N_2 + 3O_2} \tag{25.20}$$

One advantage that ozone provides over chlorine lies in the type of by-products that are formed in the process. Chlorine has the potential to react with organics present in effluent to form chlorinated organic compounds. Chlorinated organics have been monitored and controlled in discharge due to the potential negative environmental impact they present. By-products of ozone with organic compounds produce less toxic short chain acids, ketones, and aldehydes.

The major disadvantages of the ozone oxidation process are capital cost, operating cost, maintenance, and operator training. Ozone generators are costly, and facilities must purchase closed reaction vessels to handle ozone gas that might be released from solution.

Oil-Bearing Waste

Some effluents contain significant amounts of oil and grease. Oil-bearing water, in most cases, needs pretreatment before treatment for heavy metal removal. Oil/water separation requires breaking of any oil/water emulsion produced by oil and grease that is dispersed in the effluent. Oil/water separation can be accomplished by chemical emulsion breaking and separation of the oil component by skimming or techniques such as dissolved air flotation (DAF) and membrane filtration. Removal of oil also removes organic compounds that may be present in the effluent that are soluble in the oil phase.

Concentrated Metal-Bearing Effluent

Concentrated metal-bearing waste can be handled in one of three ways:

1. It can be slowly metered into dilute effluent and treated in the normal manner that dilute metal-bearing waste is handled.
2. It can be treated in batch at the source with precipitation or separation techniques such as RO or ion exchange.
3. It can be shipped off-site for treatment.

Option 2 allows treatment in the most effective manner and offers possibility for recycling the metal back into the process.

Chelated Metal-Bearing Effluent

Chelating agents can offer special challenges for reducing metal concentrations to meet discharge limits. They present the most significant problems when conventional precipitation methods are used in end-of-pipe operations. There are three options for effective treatment of chelant-metal effluent:

1. Reduction of metal to elemental form by either electrochemical or chemical reduction
2. Precipitation using an agent that can overcome the chelant-metal bonding
3. Physical separation with ion exchange or RO

A comparison of the K_{sp} and the K_f for metal-chelant formation allows the best opportunity to determine whether precipitation presents a viable option. Selecting the agent with the smallest K_{sp} gives the best hope for formation of an insoluble metal salt. Table 25.2 shows that sulfide precipitation generally provides the best choice among hydroxide, carbonate, and sulfide precipitants. In addition, polymeric precipitating agents can act as effective precipitants for metals in the presence of chelants.

Presence of chelating agents may present problems for some metal removal techniques, especially those involving formation of insoluble precipitate. Formation of metal–chelant complexes presents a stable and soluble species that needs to be broken for precipitants to act.

If chelants are suspected in effluent, it is important to measure chelant content in order to assess potential problems they may present for conventional chemical treatment methods. A total chelant test can be used for measurement of chelant content of a water sample.

Chelant concentration may be variable in effluent, and frequent testing may be required in plants that produce effluent containing both metals and chelating agents.

CHAPTER 26

Sludge Manipulation

When effluent is treated by mechanical, chemical, or biological means, solids are formed as a by-product. These solids must be removed from the water and ultimately disposed in an appropriate manner. Cost of disposal can be quite high, and removal of water through thickening and dewatering reduces disposal costs. Thus, thickening and dewatering are two common operations in effluent treatment plants.

Sludge thickening and dewatering are related, equipment-intensive operations designed to separate water from solids. Separation serves to reduce volume and weight, while increasing percent solids in the final sludge. The major difference between thickening and dewatering is the amount of water separation achieved in each process. Thickening removes only a fraction of water present in sludge, while dewatering removes as much water as possible from sludge.

The amount of water removed from sludge depends on the type of solids being treated. Water in sludge can be classified into three basic categories: free water/floc water, capillary water (bound water), and intracellular water. Each water type has a different susceptibility to removal. Free water is in the bulk fluid phase, while floc water surrounds the floc but is not attached to the solids. Free water and floc water are not constrained by adhesive or capillary forces, and are easily removed during thickening and dewatering. Capillary water is held onto the solids by capillary action and is not easily removed from sludge without chemical treatment. Use of coagulants and flocculants causes an increase in sludge particle size, and converts a portion of capillary water into free water/floc water. This release of water causes sludge to become dewaterable. Intracellular water is that portion of water that resided inside bacterial cells. This water is not dewaterable unless the cell walls are lysed or broken. Therefore, the amount of intracellular water sets the theoretical upper limit for sludge cake dryness.

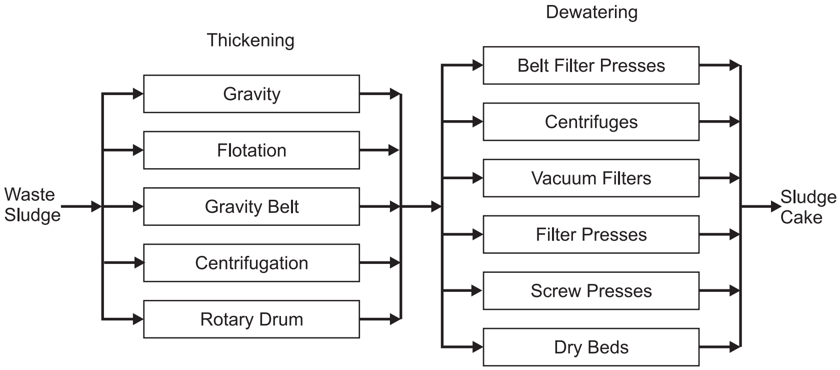


FIGURE 26.1 Conventional sludge manipulation alternatives.

For example, in a typical waste activated sludge, approximately 70% of the volume is free water, 25% is floc water, 2% is capillary water, 2% is intracellular water, and about 1% is solids. If all water except intracellular water is removed, the maximum solids achievable are only 33%. If none of the capillary water is removed, then the maximum solids attainable drop to 20%.

Common thickening and dewatering alternatives are shown in Fig. 26.1. Selection of the thickening and dewatering process depends on the type and characteristics of the sludge, and the dewatered cake disposal method employed. For example, waste activated sludge is more effectively thickened by floatation then by gravity thickening, while a belt filter press (BFP) dewaters this biological sludge more successfully than a screw press. A dewatered cake solids content that supports its own combustion is best for the most economical final sludge disposal by incineration. In some cases, the dewatering device is apparent from experience with similar sludges, or by economic or geographical constraints. In other cases, an experimental pilot program needs to be conducted, to ascertain the most economical solution to a particular sludge manipulation problem. Physical and chemical characteristics of sludge along with local considerations dictate the most technically and economically effective means for thickening and dewatering. Generally, primary or inorganic sludges produce higher concentrations in both thickening and dewatering, while gelatinous sludges such as aluminum hydroxide precipitate or waste activated sludge, produce lower concentrations in each process sequence. A sludge blending tank is typically installed ahead of thickening or dewatering machines to provide consistent sludge characteristics, when two or more different types of sludges are processed together.

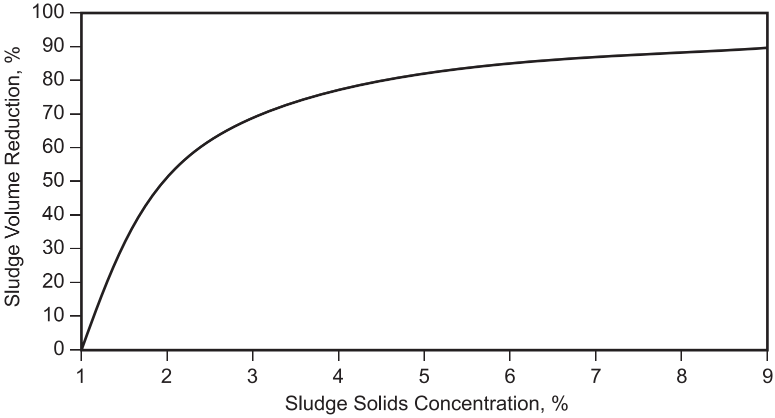


FIGURE 26.2 Sludge volume reduction by thickening.

Sludge Thickening

Sludge thickening removes free water from a slurry to reduce volume. For example, increasing the sludge solids concentration from 1% dry solids by weight to 2% reduces sludge volume by 50%, while increasing the concentration from 1 to 10% reduces sludge volume by 90% (Fig. 26.2). Thickening reduces capital and operating costs of subsequent sludge processing such as digestion, dewatering, or liquid transport (pipeline or truck), since these process costs are sensitive to the amount of water that has to be handled. In addition, other benefits including sludge flow and concentration equalization can be realized.

Primary clarifiers, flotation clarification, sludge digestion processes, and specially designed thickening units, all achieve sludge thickening in effluent treatment plants. Separate thickening is seldom practiced in treatment plants with less than about 1 mgd capacity (158 m^3/h). In this case, gravity thickening is accomplished in the primary clarifier, sludge digestion units, or both. Additional costs for separate sludge thickening in larger treatment facilities are generally justified by improved control of the thickening process and the higher concentrations attained. Higher sludge concentrations reduce capital and operational costs for subsequent sludge handling facilities to such a degree, that installation of separate thickening units is economically viable.

Gravity Thickening

Gravity thickening involves separation of solid particles from the liquid phase by gravity, just like clarification. Thickening is treating slurries having a relatively high solids concentration, and processing them to a higher solids concentration. Clarity of the water removed is of secondary importance. Clarification by sedimentation processes dilute slurries to produce clear liquor, with sludge thickening being of secondary importance. The gravity separation device should be called a clarifier-thickener, when a high effluent clarity in conjunction with maximum underflow sludge solids concentration are of equal importance, such as the secondary clarifier in the activated sludge process.

The gravity sedimentation process takes place in four basic classifications, depending on the characteristics and concentration of solids in the initial suspension. These classifications are discrete particle settling, flocculant settling, hindered (also called zone) settling, and compression settling. In continuous gravity thickeners, all four settling classifications commonly occur simultaneously, and in these cases, the thickener should be called a clarifier-thickener. For example, thickeners treating blast furnace scrubber water in the steel industry, and pulp and paper mill primary clarifiers, are actually clarifier-thickeners. The gravity thickening process works well where the specific gravity of the solids is significantly greater than that of the liquid. A typical clarifier-thickener operation in a steel mill typically more than doubles the solids concentration.

Chemical Treatment

Chemicals may aid gravity thickening. Salts of iron and aluminum have little effect on concentrating sludge or increasing dry solids flux. In some cases, these salts may improve effluent clarity. Polymer flocculants are effective aids to gravity thickening, forming larger, heavier floc particles, which settle faster and increase underflow sludge concentration. Polymers can have cationic, anionic, or nonionic surface charges, depending on characteristics of the solids involved. Effective dosages are generally in the range of 0.5 to 10 lb/ton (0.25–5 kg/tonne) of sludge solids on a dry weight basis. Two test methods are used to arrive at the best chemical program. These are the stirred thickening test, and the simple cylinder settling test. Chemical is mixed with sludge, which is placed in the cylinder and allowed to settle. Measuring the concentration of a sludge sample removed from the bottom of the cylinder and comparing it to the concentration of an untreated sample determines effectiveness of treatment.

The chemical addition point and the postdilution water rate are very important to a successful chemical application program. Suitable feed points can be after the thickener feed pumps, into the feed line immediately outside of the thickener basin, or into the center feed well. Postdilution is the addition of clean (tap) water to polymer solution after the solution has been prepared. The quantity of dilution water used has to be adjusted, so that optimum dispersion of polymer throughout the sludge volume is attained.

Flotation Thickening

Thickening by flotation is usually more effective than gravity thickening, when solids have specific gravity close to the liquid from which they are being removed, and are gelatinous, such as biological sludges from the waste activated sludge process. Dissolved air flotation (DAF) is the process used for flotation thickening and not the induced air system, which is not capable of thickening due to its turbulent surface and limited float removal capabilities. The principles and systems used for DAF thickening are the same as those for DAF clarification.

Thickening of sludges from suspended growth biological treatment processes, such as the activated sludge and nitrification processes, are efficiently thickened by DAF. Other sludges such as primary sludge, aerobically digested sludge, and sludges containing metal salts from chemical treatment have been flotation thickened, but not as commonly as waste activated sludges. Typical design parameters for DAF thickening of waste activated sludge are as follows:

Solids loading rate (solids flux)	1.5 to 2.0 lb/[h · ft^2] (7.3–9.8 kg/[h · m^2])
Hydraulic loading rate	1.5 to 2.0 gpm/ft^2 (3.7–4.9 m^3/[h · m^2])
Air/solids ratio	0.02 to 0.03 lb/lb (kg/kg)
Recycle ratio	75 to 150%
Dissolving pressure	45 to 70 psig (310–483 kPag)

DAF thickening typically yields activated sludge concentrations greater than 4% by weight and solids capture of 90% or higher.

Quality of the activated sludge has a significant effect on the final solids concentration. For example, a filamentous, bulking activated sludge may not achieve 2% solids; while 4 to 5% thickened sludge is achieved with a well biologically flocculated sludge. Sludge volume index (SVI) indicates the potential final thickened sludge concentration. Best thickening performance occurs with SVI less than 160 mL/g. Float concentration deteriorates as SVI increases beyond 200 mL/g.

DAF thickening is often augmented by addition of chemical aids, such as inorganic aluminum salts and organic polyelectrolytes. Moderate to very high molecular weight polymer flocculants have been found to be the most effective. Cationic flocculants are used in most cases, since they are particularly effective in flocculation of biological solids. Introduction of the polymer into the line at a point where bubbles are forming and contacting the solids normally produces the best results. Use of chemicals can increase float concentration and solids capture, while offsetting adverse effects of poor sludge quality when SVI is above 200 mL/g.

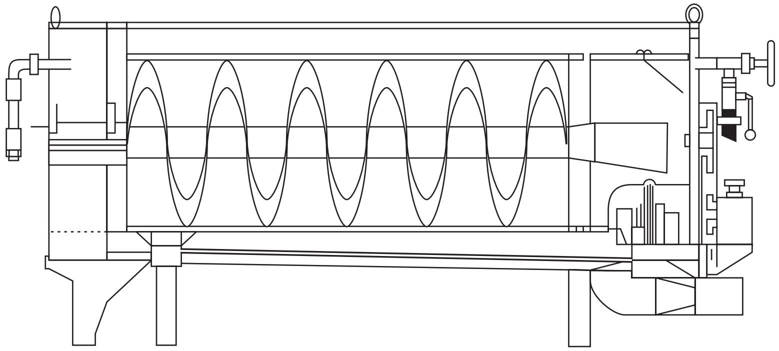


Figure 26.3 Rotary sludge thickener (RST).

Rotary Drum Thickener

The rotary drum thickener is also known as the rotary sludge thickener (RST), which consists of stainless steel or nonferrous wire mesh cloth, mounted on a cylindrical frame (Fig. 26.3). The drum revolves around its horizontal axis and is equipped with a variable speed drive, so that the rotational speed can be adjusted for the specific application. Chemically conditioned slurry flows into one end of the drum, removed free water flows through the screen, and thickened sludge exits out the opposite end of the drum. The pitch of the flights that move the sludge through the drum along with the drum speed establishes sludge retention time in the machine. Sludge depth is approximately the height of the flights. Spray headers located outside and close to the top of the drum clean the screen with high-pressure jets. Common failure of the RST is due to jets plugging, which causes the screen to blind in those sections and a reduction in thickened sludge concentration.

Organic polymer sludge conditioning is required for thickening. A RST system, therefore, consists of a chemical conditioning system including polymer makeup, chemical feed and polymer/sludge mixing facility, and the rotating drum thickener. Organic flocculants agglomerate fines in the slurry, so that free water can be readily drained through the screen. Moderate to very high molecular weight cationic polymers are used, particularly for conditioning biological sludges. Inorganic or organic coagulants may be used in conjunction with organic flocculants for specific sludges or sludge blends.

The RST system is primary used for thickening biological sludges (waste activated sludges), biological sludge mixtures, and primary sludges. Typical operating results are shown in Table 26.1.

Advantages of rotary drum thickeners are low capital cost, energy usage, and maintenance costs along with small space requirements. They are often used to increase capacity of BFPs and screw presses,

Waste Activated (Biological) Sludge	
Inlet slurry concentration	0.5–1.5%
Thickened sludge concentration	4–10%
Solids capture	95–99%
Polymer dosage	1–25 lb/ton (0.5–13 kg/tonne) dry solids
SVI < 100 produces highest concentration and uses lowest polymer dosage.	
Municipal Primary Sludge	
Inlet slurry concentration	3–4%
Thickened sludge concentration	8–12%
Solids capture	95–99%
Polymer dosage	2–8 lb/ton (1–4 kg/tonne) dry solids
Pulp and Paper Primary plus Waste Activated Sludge (WAS)	
Mixture	30–70% primary, 70–30% WAS
Inlet slurry concentration	1–4%
Thickened sludge concentration	6–10%
Solids capture	95–99%
Polymer dosage	4–20 lb/ton (2–10 kg/tonne) dry solids

Table 26.1 Rotating Sludge Thickener Operating Results

either for an existing installation or as part of a new dewatering installation.

Gravity Table Thickeners

Gravity table or belt thickeners (Fig. 26.4) are a simple means for thickening sludges. Table thickeners stem from the design of belt presses used for sludge dewatering. In belt press dewatering, effective sludge

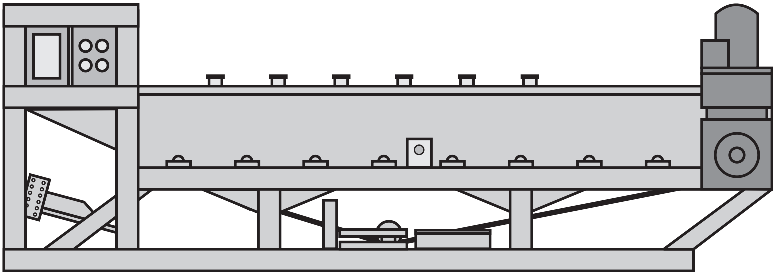


Figure 26.4 Gravity table thickener.

thickening has to take place in the gravity drainage section of the press, so that remaining sections of the press can successfully dewater the sludge. Chemical treatment of slurry before the belt thickener is required to release the maximum amount of free water from the sludge. The gravity table thickening system therefore includes a chemical conditioning system. The type of organic polymers used is the same as for the rotary drum thickener, and depends on the specific sludge.

Chemically conditioned sludge is distributed across the width of the porous belt media, (right side of Fig. 26.4) running continuously through the machine. Free water drains by gravity into a pan below the moving belt, from where it is returned to the effluent treatment process. Adjustable plows furrow and roll the sludge to prevent ponding, and expose free water to open belt areas. A low-wear grid system supports the belt and shears capillary water from the underside of the belt to increase water drainage through the belt. No pressure or vacuum assistance is needed. Thickened sludge is discharged off the end of the unit. A high-pressure shower assembly washes the belt on its return to the head end of the machine to remove particles trapped in the belt, so that maximum water drainage is accomplished during its next thickening pass. Belt speed adjustment is provided by a variable speed drive for operational optimization.

Table thickeners are used for many types of sludges including primary, biological, and mixtures of the two. Thickening results for table thickeners are similar to those achieved by rotating sludge thickeners. Table thickeners are often coupled with screw presses to increase the press capacity for dewatering dilute slurries.

Centrifugal Thickening

Solids concentration or thickening can also be accomplished by centrifugation. The three types of centrifuges used are the solid bowl (also called decanter), basket, and disk-nozzle. The solid bowl or decanter is the most commonly used type of centrifuge for sludge thickening, while the basket type is used for thickening smaller quantities of sludges.

Solid Bowl (Decanter) Centrifuges

Operating parameters and their interaction in the centrifugal process for liquid/solids separation using solid bowl or decanter centrifuges are discussed in detail later in this chapter. The principal operational variables include characteristics of the feed sludge; SVI for waste activated sludge thickening; bowl rotational speed; slurry feed rate; liquid pool depth in the bowl; differential speed between the bowl and the conveyor; and need to add polymers to improve performance. Interrelationships between these variables are different for each specific installation. Generally, bench scale or onsite pilot plant tests are used to determine appropriate machine size and operating parameters for a specific location.

Solids capture is important when thickening to minimize the amount of solids returned to the treatment process. Many systems are designed with standby polymer systems for use when capture rates have to be increased. Percent capture is calculated by:

$$\text{Percent Solids Capture} = \left[1 - \frac{C_r(C_c - C_s)}{C_s(C_c - C_r)}\right]100 \tag{26.1}$$

where C_r = concentration of solids in reject liquor (centrate), mg/L or %
C_c = concentration of solids in cake, mg/L or %
C_s = concentration of solids in slurry feed, mg/L or %

Basket Centrifuge

The basket-type centrifuge is a batch operation that limits its application to small flows for thickening and dewatering. The basket centrifuge is more generally used for sludge dewatering, and details of its operation are discussed in the Sludge Dewatering section. Sludge characteristics, slurry feed rate, bowl speed, and duration of sludge removal affect the extent of thickening and solids capture. As with the solid bowl, a standby polymer system is generally included in the installation to increase solids capture when needed.

Disk-Nozzle Centrifuge

The disk-nozzle centrifuge, while primarily a liquid/liquid separation device, can be used to thicken slurries. It is suitable for thickening slurry with very fine, uniform particle size, since it creates greater centrifugal force than a solid bowl or basket centrifuge. It has been used for thickening biological slurries such as waste activated or similar sludges. The disk-nozzle centrifuge effectively thickens waste activated sludge at high feed rates and without polymer addition due to its high gravitational force.

Slurry is introduced into the center of the machine at the top and is distributed between the stacked conical disks (Fig. 26.5). Disks are stacked so that the space between them is 0.1 to 0.25 inches (2.5–6.4 mm) apart. Solids settle to the underside of the disks and slide down the plates to the bowl wall, where compaction takes place due to the gravitational force. Concentrated solids are discharged through nozzles in the periphery of the rotating bowl. Centrate passes under the sludge and discharges from the center of the centrifuge. The disk-nozzle centrifuge is subject to frequent plugging when coarser solids are encountered, due to the close spacing of the disks and the small nozzle size. Slurries containing coarse solids are typically screened before introduction into the machine.

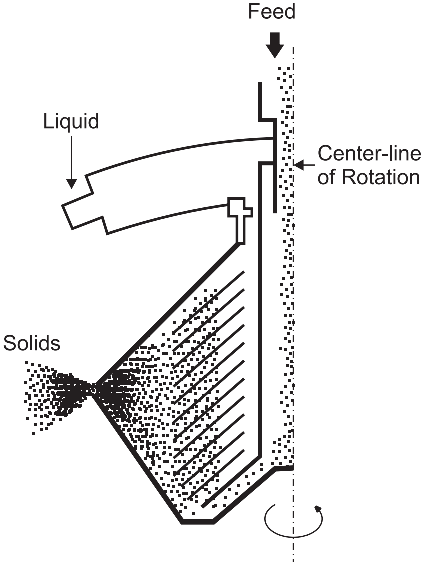


Figure 26.5 Disk-nozzle centrifuge.

Sludge Dewatering

Sludge dewatering is normally the final liquid/solids separation step in an effluent treatment process. The dewatering method is often dictated by the nature of solids being dewatered, final method of sludge disposal, and specific local conditions. The goal is to produce a dewatered sludge cake of such density, solids content, and strength, to meet subsequent sludge disposal requirements. For example, maximum water needs to be extracted from sludge if it is going to be incinerated to minimize use of auxiliary fuel. Low cake moisture (high solids concentration) can be required to pass cake drainage tests for landfills and minimize hauling costs. Sludge may not need to be dewatered to such a high extent when cake is used for a land reclamation program.

Nature of Sludge

The nature of sludge refers to both physical and chemical sludge characteristics. Viscosity, volatile (organic) content, compressibility, and particle size, shape, density, and electrical surface charge are included. Typically, some of these are design considerations and out of the effluent treatment plant operational control. Parameters within plant control include feed solids concentration, accumulation of fines, sludge age, and biological health.

Feed Solids Concentration

A change in feed solids concentration can affect solids capture, cake solids, polymer dosage, and sludge throughput of the dewatering device.

The primary clarifier operation, upstream sludge thickening facilities, or sludge blending tank, need to be operated so that as consistent a sludge solids concentration is provided to the dewatering device as possible, to avoid continuous adjustment of machine operating parameters and chemical addition.

Accumulation of Fines

The level of fines recycled back to the treatment plant is minimized by a high solids capture by the dewatering machine, and prevents them from accumulating in the plant. The particle size distribution in the sludge changes if fines cycle up in the plant, resulting in increased chemical consumption, wetter cake, and further reduction in solids capture. Fines can also upsetother treatment plant processes such as aeration, clarification, and biochemical oxygen demand (BOD) removal.

Sludge Age

Sludge age in one context refers to the time sludge spends in the effluent treatment plant before dewatering. Prolonged aging periods often alter sludge characteristics through anaerobic decomposition of organic matter or chemical reactions that increase the quantity and sometimes even the type of chemicals needed for conditioning. This aging period needs to be kept as short as possible, so that fresh sludge is always available for dewatering.

In biological treatment processes, sludge age indicates the time sludge is under aeration, which affects sludge dewaterability. Older sludge can result in wetter cake, lower hydraulic and solids throughput, and higher polymer demand. Very young sludge age can also be problematic for dewatering and commonly requires high chemical dosage.

Secondary Sludge Biological Health

One of the first variables that are suspect when problems occur while dewatering secondary treatment sludge is the biological health of the sludge. High SVI for biological sludge indicates difficult sludge to dewater, just as it indicates the sludge is difficult to settle. “Unhealthy” sludge caused by toxins, excessive age, insufficient nutrients, improper dissolved oxygen levels, or imbalanced food to mass ratios dewaters poorly, often increasing polymer requirements, reducing throughput, and producing wetter cake.

Belt Filter Press

The BFP (Fig. 26.6) is also referred to as a twin belt press or a twin wire press, particularly in the pulp and paper industry. The BFP generally employs two moving porous belts to dewater slurries (sludge) to a moist cake.

Centrifugation

Centrifugation has long been used for dewatering as well as for thickening sludge. Selection of the proper centrifuge is important, since

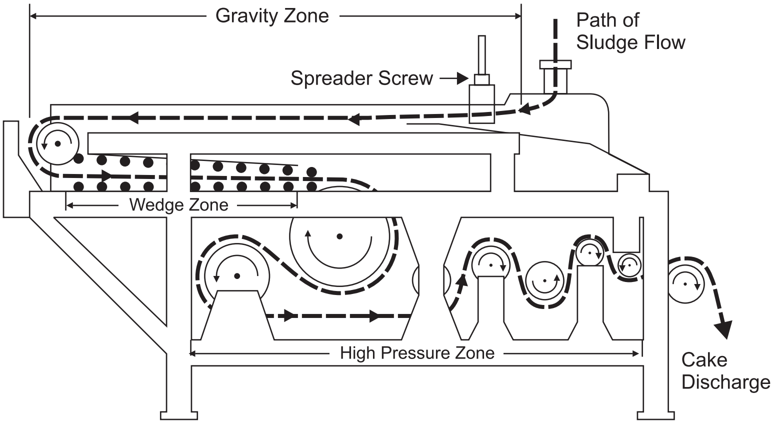


Figure 26.6 An illustration of a BFP, Andritz-Ruthner, Model S-7.

design characteristics can be tailored to meet specific application needs. Several inherent advantages in centrifugation make it attractive for many dewatering applications. Among important advantages are compact design, completely enclosed machine, high throughput, and relative simplicity of operation. They can be installed and operated outdoors in moderate climates.

Vacuum Filters

Rotary vacuum filters have been used for many years by industry and municipalities to dewater waste sludges. They are also used in many process applications such as dewatering slurries in the chemical industry, pulping operations in paper mills, and coal recovery and ore processing in the mining industry to name a few. Solids content of dewatered cake varies considerably, depending on the type of slurry being dewatered and particle size. Slurries of inorganic solids may dewater to 80% solids, whereas a biological sludge may dewater to only a 20% solids level.

The principal component of the continuous vacuum filtration system is the cylindrical filter drum enclosed at both ends. The drum supports a porous medium or cloth and rotates while partially submerged in a slurry vat. The interior surface of the drum is divided into compartments by partitions (seal strips) that are connected by pipes to a valve located at one end of the drum. The valve controls application of vacuum to specific areas of the filtering medium. The valve allows each compartment to function continuously in the following sequence as the drum rotates (Fig. 26.7).

1. *Cake formation*: The drum is submerged in the vat containing slurry, and vacuum is applied during this step. The first solids that collect on the medium act as a filter for subsequent cake formations. For this reason, it is desirable that cake be formed gradually to the optimum thickness.

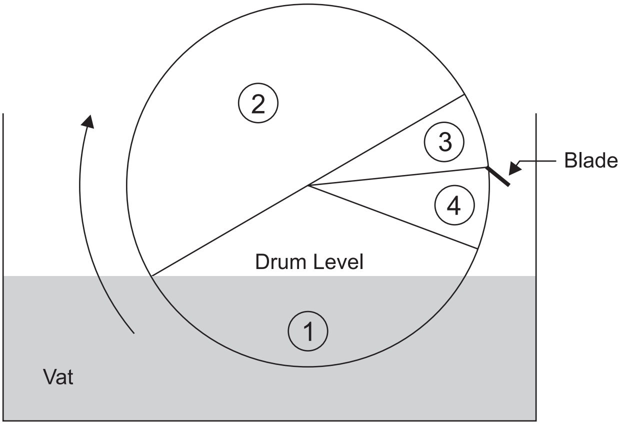


FIGURE 26.7 Operating sequence of rotary drum vacuum filter.

2. *Liquid extraction or drying*: Vacuum is also applied during the liquid extraction or drying step. Water or liquid is drawn out of the filter cake through the filter media to the inside of the drum, through the valve, and to the receiver through a vacuum line separate from the cake formation vacuum line.
3. *Filter cake removal or discharge*: Removal of filter cake from the drum is accomplished by one of several methods depending on the type of vacuum filter, which will be discussed later.
4. *Media washing*: The final step in the cycle of vacuum filter operation can be accomplished on a continuous or intermittent basis. High-pressure water sprays are normally used to dislodge particles that could buildup and clog the filtering medium. It often becomes necessary to acid wash the filter media on a routine basis, when ferric chloride and lime are used as conditioning chemicals, or if the slurry contains oils or greases.

Screw Presses

Screw presses are used almost exclusively in the pulp and paper industry. The screw press needs compressible solids (like fibers) in the slurry for efficient dewatering performance. Screw presses do not dewater slurries well without some compressible solids in the sludge. Fiber recovery in some mills has improved to a point where screw presses fail to function well due to the lack of fiber in the effluent sludge. In these cases, either some fiber is sent to the dewatering process, or replacing the screw press is required. Addition of sawdust generally does not improve screw press operation, since sawdust is not a good substitute for fiber.

The screw press dewaters pulp and paper mill primary or blended primary, and biological (secondary) sludges to yield cake solids in the 26 to 52% range, depending on the ratio of biological sludge to primary

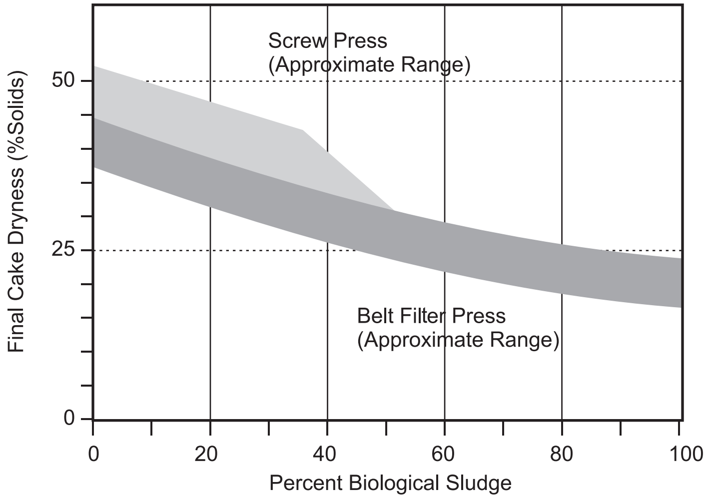


Figure 26.8 Application of screw press for blended sludges.

sludge (Fig. 26.8). Operation of screw presses on blended sludges containing as much as 50% biological solids is difficult. The feasibility of using a screw press on blended sludges having 50% or more biological solids is questionable. Other dewatering devices, such as BFPs or decanter centrifuges, are better applications then the screw press for blended sludges with a high percentage of biological solids.

The basic components of the screw press are shown in Fig. 26.9, and include:

- The headbox serves as the sludge inlet to the press. The headbox was only a few feet (about 1 m) high for early presses operating on primary sludge. The headbox for newer presses can be as tall as 10 to 15 feet (3–4.6 m), especially when dewatering blended primary and biological sludges.

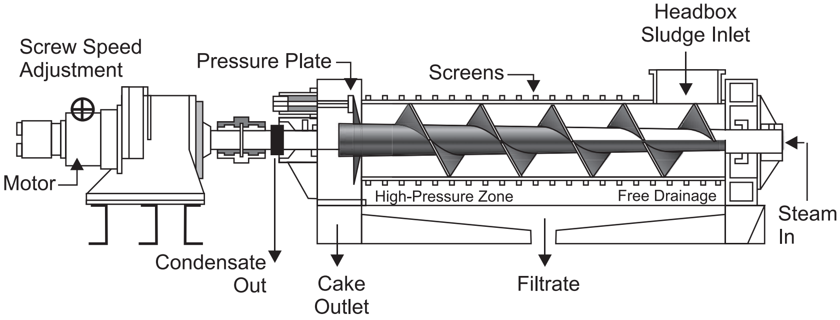


Figure 26.9 Cross section of a typical screw press.

- The barrel screen section through which the pressate water flows is divided into four sections along the length of the machine:
  1. Free drainage section immediately below the headbox
  2. Initial- and medium-pressure sections
  3. High-pressure section
  4. Plug section that develops the choke pressure
- A tapered shaft has a small diameter at the inlet end of the machine and increases to a maximum diameter at the cake outlet with helical conveyor flights (helical screw) attached to the shaft. The increasing diameter of the shaft creates a radial pressure on the sludge between the shaft and the barrel screen section as it is moved through the machine by the screw conveyor.
- Low-pressure steam is sometimes introduced into the shaft to reduce water viscosity to improve drainage and heat the sludge to achieve some evaporative drying after the cake has been discharged from the press. This is not cost-effective unless waste steam is used, even though a dryer cake is achieved.
- The helical flights on the shaft are cylindrical, not tapered, and have a very close clearance to the barrel section to keep the screen openings clear. This clearance is typically about 0.02 to 0.04 inch (0.5–1 mm).
- One or sometimes two of the last helical sections of flights are cut off to create a plug at the end of the screw. This plug creates the necessary high backpressure on the sludge being conveyed forward.
- A pressure plate or spring-loaded doughnut applies final pressure at the press outlet. It pushes against the plug that is being forced out of the press by the rotating screw shaft. It also breaks up cake exiting the machine, so that it does not plug the outlet.
- Cake exits the press into the outlet box.
- A variable speed motor drives the shaft and controls the shaft rotational speed.

Plate-and-Frame Filter Presses

The principle of plate-and-frame press dewatering (Fig. 26.10) is similar to that for vacuum filtration except that pressure, not vacuum, is used to separate the slurry, and batch, not continuous, operation is used. Fluid pressure generated by pumping slurry into the unit provides the driving force. Plate-and-frame presses are also referred to as

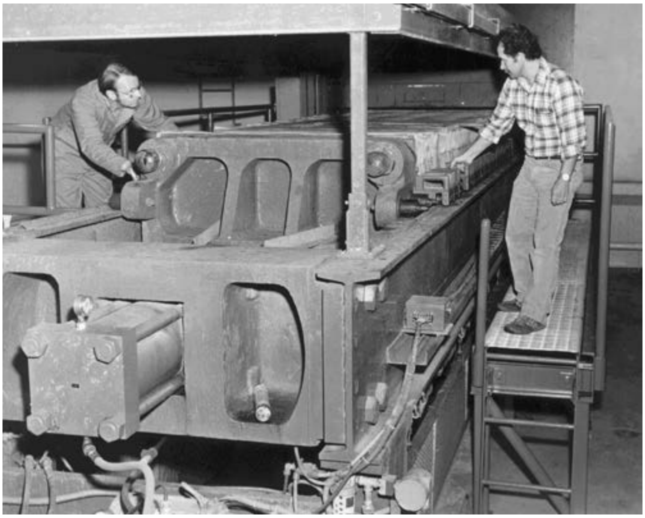


Figure 26.10 Plate-and-frame press dewatering sewage plant sludge.

recessed chamber presses and diaphragm presses. The press consists of vertical plates with recessed chambers held in a frame and pressed together between a fixed and moving end. Each plate is fitted with a medium, normally woven monofilament polypropylene filter cloth because of its resistance to blinding, ease of cleaning, and durability.

Plate-and-frame presses do not close to squeeze or press sludge. Instead, sludge pumps capable of developing pressures up to 225 psig (1.6 MPag), force sludge into the media-lined cavities between vertical plates. Presses for dewatering sludges are generally designed for a maximum pumping pressure of 100 psig (689 kPag). Filtrate flow is initially high as the press fills and then starts decreasing as dewatering progresses. Ultimately, filtrate flow stops or the cycle time (determined by experience) expires, the sludge pump is shut down, the feed line drains, and the press begins to unload. The moving end or the press retracts and separates the plates, allowing filter cake to fall from the plates. Usually, presses are equipped with an automatic gear arrangement to open and separate the plates. After cake has been removed, the moving end pushes the plates against the fixed end for recharging to complete the cycle (Figs. 26.11–26.14). Plates are generally washed between cycles with a high-pressure hose to prevent cloth blinding on succeeding runs. Typical cycle times range from 1 hour to 24 hours, depending on the process and equipment sizing. Presses are commonly installed above floor level, so that a hopper can be placed beneath the press to collect dry cake. Plate-and-frame presses are not as widely used as other mechanical dewatering devices, since they are a batch process while others are a continuous process.

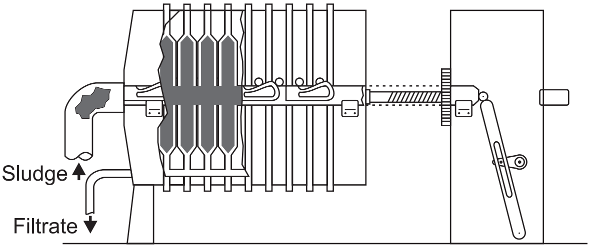


Figure 26.11 Plate-and-frame press charging. With plates closed, sludge is pumped into the press. The cake begins to form and becomes the filtering medium. Filtrate flow rate is highest at the start of the cycle.

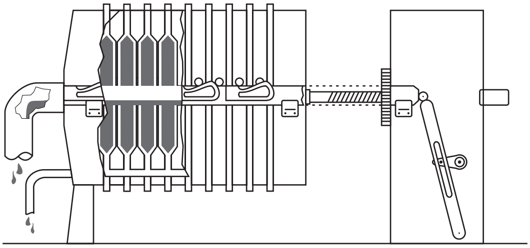


Figure 26.12 Plate-and-frame press draining. When cakes are formed and filtrate flow is reduced, the pump is automatically stopped and the inlet line drained.

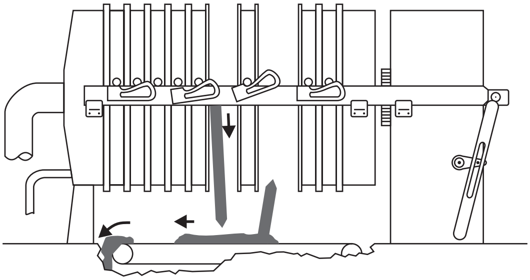


Figure 26.13 Plate-and-frame press discharging. The traveling end of the press retracts. A reciprocating mechanism automatically separates plates in sequence. Filter cakes drop and are carried away by a conveyer.

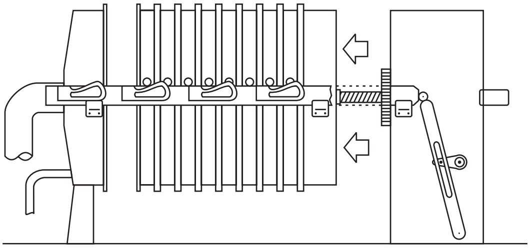


Figure 26.14 Plate-and-frame press closing. After the last cake has dropped, the plates are pressed together for another filtering cycle.

The variable volume recessed plate filter press (Fig. 26.15), differs from the fixed volume press, in that it utilizes a flexible membrane or diaphragm to provide a second squeezing phase to sludge within each chamber after filter cake formation. The space between the press plate and its flexible membrane is filled with water to provide additional compression of the sludge at a predetermined filter press feed pump pressure. The variable volume press is generally called a diaphragm press.

Drying Beds

Drying beds are often used to dewater waste sludges, where land is available and climatic conditions are favorable. In early designs, sand was used as the filtering medium. The typical sand bed has tile

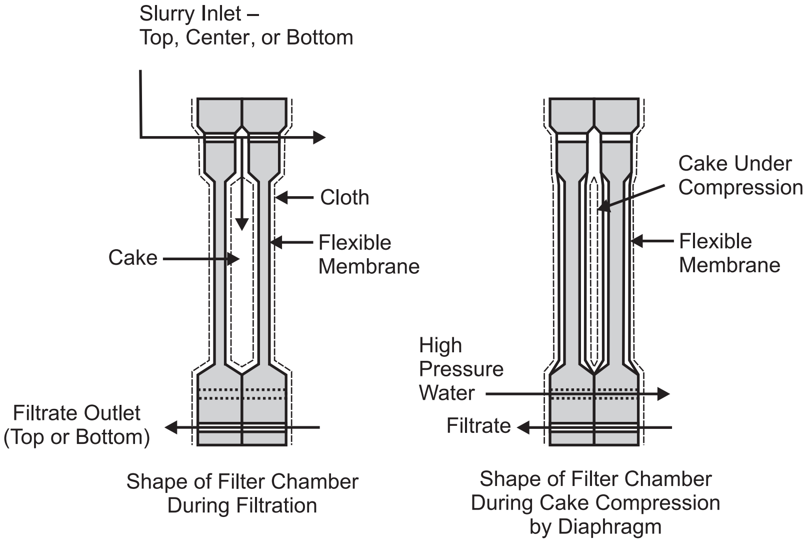


Figure 26.15 Variable volume (diaphragm) filter press.

Figure 26.16 Conventional sand drying bed with tile underdrain system, shown here during construction.

underdrains covered by 12 inches (305 mm) of graded gravel, then topped with 6 to 9 inches (152–229 mm) of 0.3 to 1.2 mm sand, with a uniformity coefficient less than 5.0 (Fig. 26.16).

Under the right circumstances, the drying bed provides advantages over mechanical dewatering devices such as low operating costs due to low energy requirements, little maintenance, and minimal operator attention. They have the ability to handle variable sludges and to produce drier cakes than most mechanical devices. There are, however, limitations to their use, such as high land requirements and weather dependency. Since drying beds are outdoors, odor may be a problem, if the sludge is high in organic matter.

For effective dewatering on drying beds, sludge must have physical properties that allow drainage of contained water without blinding of the filtering medium. Water drainage should be rapid and relatively complete, reducing to a minimum the residue that must be evaporated. Sludge applied to the drying bed should be as thick as possible to reduce required drying time. Chemicals that improve release of free water have proven effective in speeding drainage and significantly reducing drying time.

Drying beds have been popular for dewatering municipal sewage sludges, including primary, aerobically or anaerobically digested, and mixtures of primary with biological sludges. Many other types of sludges are dewatered on drying beds, including water plant clarification sludges, lime softening sludges, and industrial sludges.

Drying bed designs generally fall into the following categories: impervious bottom beds, impervious bottom with drainage strips, sand beds, and sand beds with multiple cement tracks to provide complete mechanical unloading.

Simple impervious bottom beds and those with drainage strips are relatively easy to install and maintain, but they require longer drying times due to the reduced water drainage. Originally, sand beds were designed with clay tile as the underdrain system. Clay tile tended to break easily, ruling out the use of mechanical equipment for dry sludge removal. In addition, sludge removal with mechanical loaders has caused relatively high sand losses, which can be an important consideration if sand is scarce.

Some plants have been successful with resilient plastic underdrain tile and specially designed buckets to skim off dry sludge from the sand. One bed using alternating sand and cement strips throughout the entire bed, coupled with a drive-down ramp across the full width of the bed, allows a front end loader to make parallel passes when removing dried sludge. Cement strips spaced at tire track distances prevent the bucket from digging into the sand media. This bed appears to offer the advantage of hard surface support along with open sand drainage. The use of polymer significantly increases dewatering speed and therefore reduces the area required.

Where sand beds are already in place, polymer addition allows more complete drying and reduces the volume of dried sludge for disposal. Surface loading rates can often be two or more times as great as on beds not using polymer dewatering chemicals.

Sludge application largely depends on local plant needs and the type of bed used. Normally, sludges are applied from 6 to 10 inches (152–254 mm) deep, depending on local conditions and the amount of sludge available for drying. Addition of new sludge on top of partially dried sludge is not recommended. An exception to this may be thin digester supernate, which is sent to the drying bed first in order to minimize its impact on the primary clarifier. In this case, chemicals must be used in order to prevent blinding of the drying bed by multiple sludge applications.

CHAPTER 27

Emulsion Treatment

Water and oil sometimes combine (emulsify) during industrial processes. Resulting emulsions are either oil-in-water (o/w) or water-in-oil (w/o), depending on which material is dispersed in the other. An o/w emulsion has water as the continuous phase, while the w/o emulsion has oil in the continuous phase. Either type of emulsion may contain other contaminating materials (solids, dirt, metal particles, emulsifiers, cleaners, soaps, solvents, etc.).

Emulsions can be found in a variety of industries and formed by a variety of processes. Since formation of emulsions is so specific to the industry and process, emulsion breaking product selection is somewhat difficult and requires bench testing. Oils themselves vary greatly in composition, ranging from lubricating and machining oils, to soluble oils, rolling oils, animal oils, and occasionally aromatics.

Industries where emulsions are commonly found include:

- Basic metal industries—steel hot strip mills, casting systems, and aluminum
- Automotive and machining industry—metalworking and metal parts manufacturing waste oils such as lubricating oils, cutting oils, lapping compounds, grinding fluids, and specialty fluids
- Petroleum refining industry—slop oils from separator skimmings, tank bottoms, and coke plants
- Petrochemical industry—olefin quenching operations
- Textile mills/synthetic fiber industry—spin finishing mills
- Meat and food processing industry—rendering plants, creameries, breweries, and canneries
- Paints, surface coatings, and adhesives industries
- Oils, fats, and waxes industries
- Soap and detergents industry including laundries
- Leather industry

Theory of Emulsions

To understand emulsion breaking requires an understanding of emulsion stability. The emulsion is generally stabilized by one or more of three basic mechanisms: ionization, adsorption, and frictional contact.

Ionization is caused by surface-active chemical agents in a system. Surfactant molecules usually carry an ionic charge and seek out the oil–water interface at the surface of the emulsified droplets.

Adsorption stabilization is caused by fine particles adsorbed at the oil–water interface that tend to reinforce the interfacial film. Dispersed droplets thus cannot coalesce because of the interference, or blocking effect, caused by the solids. Electrostatic charges may also be present and play a significant role in emulsion stabilization.

Frictional contact stability occurs when oil and water phases mix with each other. Vigorous agitation is required to form the emulsion. In this case, coalescence of oil is hindered due to the inability of the oil or water to drain with sufficient speed to allow for the collision of two particles. Electrostatic charges can arise from this mechanism, and again tend to collect at the oil–water interface. This gives rise to a stable emulsion due to repulsion of charged emulsified droplets.

In emulsion theory, a double layer of electrostatic charge (the Helmholtz layer) is formed around a spherical emulsified droplet. The surface of the emulsified droplet takes on a characteristic charge, while the outer surface of the Helmholtz layer has a concentration of opposite charge. The Helmholtz double layer model is shown in Fig. 27.1. The emulsified spherical particle has attained a characteristic surface charge, causing the layer just outside to acquire an opposite charge. These charges repel other particles having the same charge, giving rise to emulsion stability. In nearly all cases, surface charge on the droplet is negative.

In destabilizing or breaking emulsions, stabilizing factors must be eliminated or neutralized to allow emulsified droplets to coalesce and the emulsion to resolve. Accumulated electrostatic surface charges associated with an emulsified droplet can be neutralized by introducing an agent having an opposite charge to that of the droplet. Chemical emulsion breakers work on this principle to destabilize and resolve emulsions.

Two types of emulsions occur:

1. Oily waste emulsions—oil dispersed in a continuous water phase
2. Waste oil emulsions—water dispersed in a continuous oil phase

The two types of emulsions can be distinguished by observation. An oily waste emulsion is water continuous, and appears to be oily,

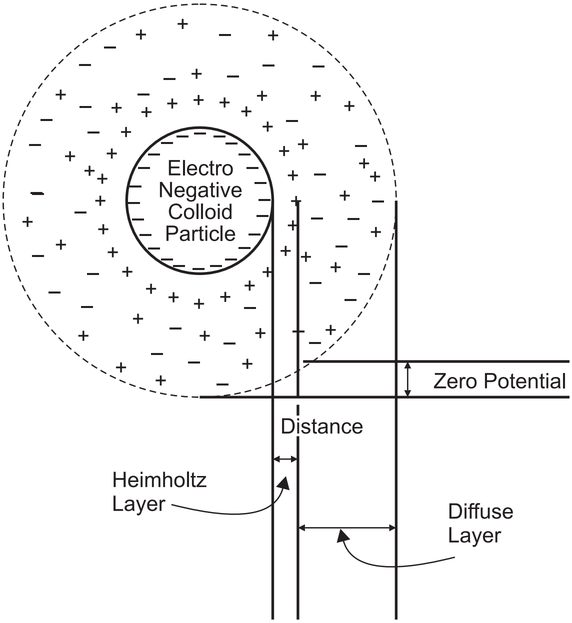


Figure 27.1 Electrical charge distribution of emulsified particle.

dirty water. A drop of oily waste emulsion disperses in a beaker of water upon gentle stirring. A waste oil emulsion is usually thick and viscous, and when a drop of it is placed in water, it remains as a discrete drop (Figs. 27.2 and 27.3).

Figure 27.2 A few drops of oily water (o/w emulsion) when added to water will disperse in the water.

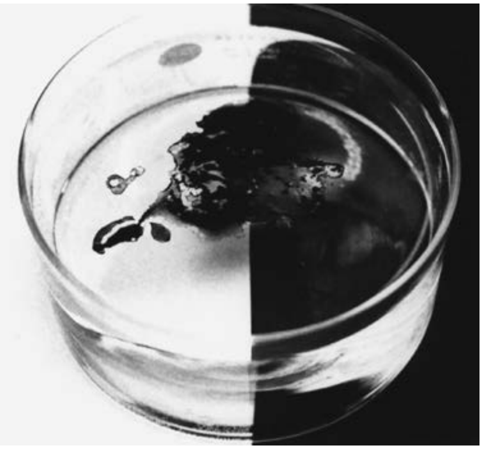


FIGURE 27.3 A few drops of oily water (w/o emulsion) when added to water will remain as a separate phase floating on the surface of the water.

Oily Waste

An oily waste emulsion (o/w) may have an appearance from black to gray, oily, dirty water. Adding an oily waste into water results in the emulsion dispersing into the clean water, forming an oily effluent that is less concentrated than the original emulsion. An oily waste emulsion may contain any of various types of oil in a wide range of concentrations. These oils are defined as substances that can be extracted from water by hexane. In addition to oils, typical contaminants of these emulsions may be solids, silt, metal particles, emulsifiers, cleaners, soaps, solvents, and other residues. The type of oils found in these emulsions depends on the industry. They may be fats, lubricants, cutting fluids, heavy hydrocarbons such as tars, grease, and crude oils and light hydrocarbons such as gasoline, kerosene, and jet fuel. Their concentration in effluent may vary from only a few mg/L to as much as 5–10% by volume. Treating the emulsion is usually accomplished using coagulants dosed at an appropriate level to neutralize the electrostatic charge stabilizing the emulsion.

Oily waste (o/w) treatment generally uses gravity separation of nonemulsified (free) oil and chemical treatment, and separation of emulsified oil by air flotation processes. However, other more sophisticated methods [reverse osmosis (RO), ultrafiltration (UF), and activated carbon adsorption] are available and can be effective. Gravity separators reduce the amount of suspended particulate matter through settling, and enable nonemulsified oil to rise to the surface. Skimmers in the separator remove free oil for further treatment. Air flotation, using either the dissolved or the induced method of introducing air bubbles into the liquid, helps oil and solids float to the surface as a sludge, where they are skimmed off for further treatment.

Waste Oil

Waste oil emulsions are typically black viscous liquids, where oil is the major component of the emulsion and water is the minor component. When a drop of w/o emulsion is added to water, the emulsion droplet remains intact and does not disperse. Since oil is the major component of the emulsion, emulsion breaking is usually performed for the purpose of oil recovery. W/O emulsions can be broken by chemical or physical methods such as heating or centrifugation. Centrifugation breaks oil emulsions by separating oil and water phases under the influence of centrifugal force. Typically, physical methods alone are not efficient in resolving these emulsions.

Waste oil emulsion terminology varies from industry to industry. Waste oils are also called slop oil, trap oil, floc oil, and skim off. Other forms of w/o emulsions include oily sludge, dissolved air flotation (DAF) sludge, and separator skimmings. Oil skimmings are chemically stabilized emulsions due to coagulants and flocculants needed to remove oil from water.

Waste oil treatment involves recovering oil from an emulsion, using one or more of four common treatment methods: treatment by transfer, pH adjustment, internal mixing, and chemical treatment. Batch processing of the emulsion is common to all four methods. Application of heat and chemicals during processing is often required to reduce viscosity, aid in mixing of treatment chemicals, and neutralize electrostatic charges stabilizing the emulsion. Solids are often a part of the emulsion and need to be addressed during chemical treatment. The emulsion destabilizing chemical plays a key role in separating oil from water and is often chosen based on bench testing.

Emulsion Treatment

Oil separation can be divided into three basic processes: chemical, mechanical, and thermal. Elements of all three are required for efficient emulsion separation.

Chemical Treatment

Chemicals are commonly used for treatment of oily effluents and are used to enhance mechanical treatment and separation. In resolving emulsions, stabilizing factors must be neutralized to allow emulsified droplets to coalesce. Electrostatic charges on emulsified droplets are neutralized by introducing an oppositely charged chemical. Emulsion breakers provide this opposite charge and are most often combined with mechanical and thermal treatments to achieve the best separation.

Oil-in-Water Treatment o/w emulsions are typically treated using cationic coagulants. These coagulants can be organic, inorganic, or blends of both (Fig. 27.4). Since emulsions are highly variable, bench testing is recommended to determine the correct chemical treatment for the emulsion. Surface area of the emulsified particles can be very high, and

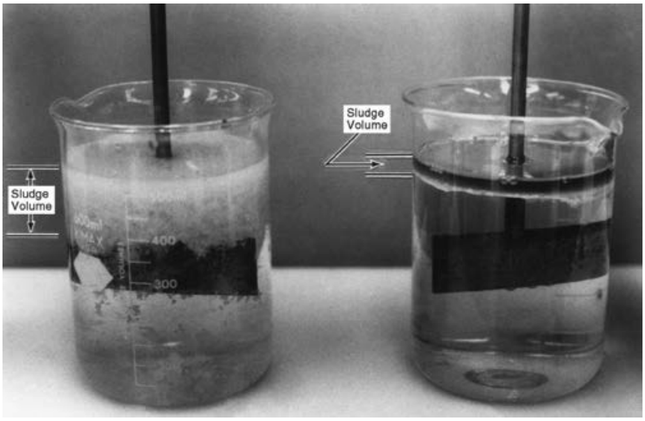


Figure 27.4 The use of organic emulsion breakers in place of alum or salts, which form hydrous flocs, greatly reduces sludge volume. The oil can be extracted from the sludge.

coagulant dosage is directly dependent on particle size and concentration. Coagulant dosages range from a few mg/L to 1000s of mg/L.

While good screening of coagulants is recommended, basic coagulant families are commonly used:

- DADMAC—diallyldimethylammonium chloride
- epi-DMA—epichlorohydrin-dimethylamine
- Aluminum-based chemistries—polyaluminum chloride (PACl)
- Aluminum-DADMAC blends
- Aluminum-epi-DMA blends
- Starch-based coagulants
- Iron-based coagulants

Water-in-Oil Treatment Waste oil emulsions typically require emulsion breakers that are soluble in hydrocarbons. These include ethyleneoxide-proplyeneoxide (EOPO) polymers and oxyalkalated resins and sulfonates. These chemistries neutralize electrostatic charges. Addition of these chemistries is often accompanied with heating waste oil to aid in mixing and the final resolving of water and oil layers. Chemical dosage can range from 100s of mg/L to 1000s of mg/L, depending on the emulsion (Fig. 27.5). Waste oil emulsions may have a significant amount of solids. Flocculating these solids with a medium to high cationic charge flocculant, helps resolve the emulsion into three layers: water, solids, and an oil layer. Chemical programs are normally applied in batch treatment tanks, and these tanks are usually equipped with internal mixing such as electric propeller mixers.

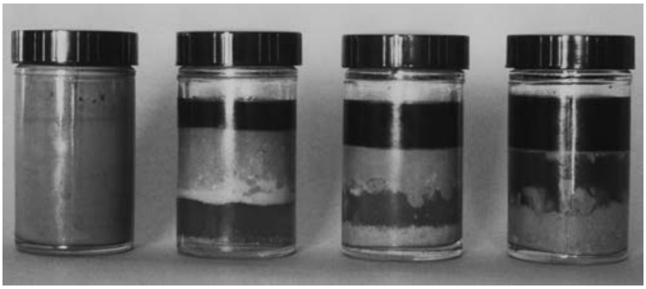


Figure 27.5 Breaking a waste oil emulsion with a chemical emulsion breaker showing the effect of increasing chemical dosage on maximizing oil recovery and solids separation.

Mechanical Treatment

Mechanical treatment of emulsions includes DAF, induced air flotation (IAF), and settling in special separators for the refining industry called corrugated plate interceptor (CPI), and American Petroleum Institute (API) separator. Details of the equipment are presented below.

Thermal Treatment

Thermal treatment of emulsions has a twofold purpose. First, increase in temperature reduces viscosity of the mixture, allowing faster film flowing and separation of water from oil. Secondly, increase in temperature allows for better chemical mixing and neutralization of the stabilizing factors of the emulsion. Thus, increasing the temperature of an emulsion does help resolve the emulsion. However, heating an o/w (oily waste) emulsion has less of an effect on emulsion breaking than when a w/o (waste oil) emulsion is heated.

Separation Equipment

Additional equipment information can be found in Chap. 22 on Primary Effluent Treatment.

Oil-in-Water Emulsions

Oil separation and removal can be divided into two basic processes: gravity separation of nonemulsified oil and chemical treatment and separation of emulsified oil.

Equipment for oily waste treatment includes flotation (DAF and IAF), ultrafiltration , activated carbon adsorption, pressure leaf filtration, and RO. These systems are used to break emulsions and separate emulsified oil from the waste flow. They are typically used with some form of chemical treatment.

Gravity Separation

The primary function of gravity separators is to remove free oil from effluents; however, such separators cannot remove soluble impurities or break emulsions. Gravity separators depend on density differences and the resulting buoyant forces, to cause droplets of free oil to rise to the surface. Theoretically, oil droplets rise linearly as predicted by Stokes' law. In practice, turbulence and short-circuiting are common operational challenges with gravity separators.

American Petroleum Institute Separator The API separator consists of a rectangular trough or basin in which effluent flows horizontally, while oil droplets rise vertically to the surface (see Fig. 27.6). Free oil that collects on the surface of the separator is skimmed off and routed to storage.

API separators are designed to separate oil droplets of 0.15 mm or larger. Ideally, separators are designed within the following limits:

- Horizontal velocity should not exceed 3 ft/min (0.91 m/min)
- Separator depth between 3 and 8 feet (0.91–2.4 m)
- Depth to width ratio of 0.3–0.5
- Widths should be between 6 and 20 feet (1.8–6.1 m)

Corrugated Plate Interceptor Separator The CPI consists of packs of 12 to 48 corrugated plates mounted parallel to each other at distances of 0.75 to 1.5 inches (19–38 mm). As effluent flows between the plates, lighter oil globules float upward into the corrugation peaks, where they coalesce and move up the plates to the top of the plate pack and then to a floating oil layer at the surface (see Fig. 27.7).

Gravity Separator Performance Several factors affect performance of gravity separators, including:

- Flow rate through separator
- Turbulence or short-circuiting
- Temperature

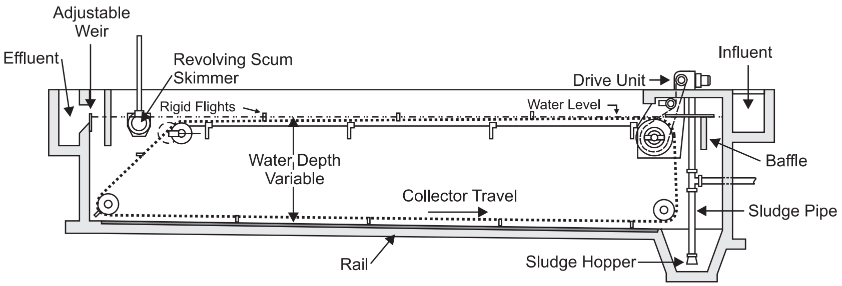


Figure 27.6 API separator. (*Courtesy of Envirex Inc., a Rexnord Company.*)

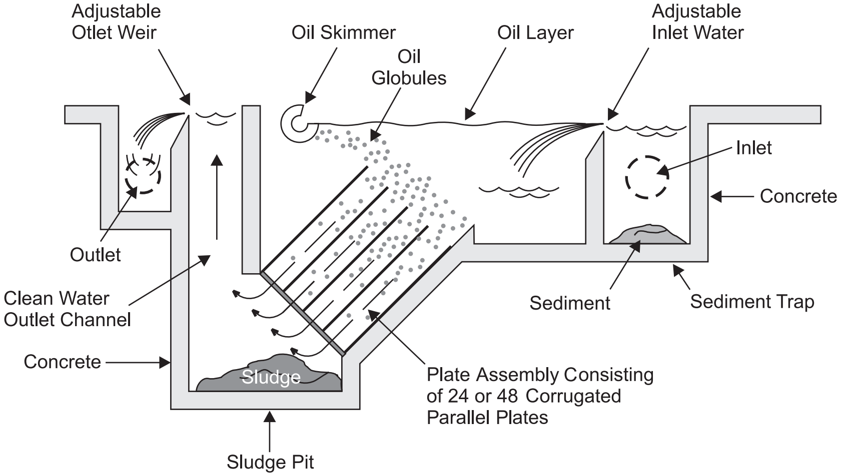


FIGURE 27.7 CPI separator.

- Effluent pH
- Specific gravity of oil
- Specific gravity of effluent
- Amount of settleable solids present
- Concentration of emulsifying agents

Figure 27.8 illustrates the separation process in an API or CPI separator. Effluent flows left to right and includes dense grit, dirt, and other insoluble matter, free nonemulsified oil, and stable emulsified oil. Suspended particulate follows a settling gradient depending on specific gravity and flow rate. Free oil similarly follows a rising gradient depending on specific gravity and flow rate. Generally, free oil includes entrapped oil-coated solids and emulsified water. API skimmings, which are generally referred to as slop oil, require treatment before they can be reused since they contain solids and water in excess of 1%, where 1% water is generally considered the acceptable limit for reuse without treatment.

Table 27.1 illustrates expected effluent concentrations and removal efficiency in a refinery effluent treatment process using an API or CPI separator.

Air Flotation Separation

Air flotation has been used for many years to treat effluents by separating solids, oils, grease, fibers, and other low-density solids. Air flotation is also used for thickening activated and flocculated chemical sludge. This section deals with flotation for the purpose of clarification of suspended oil and solids.

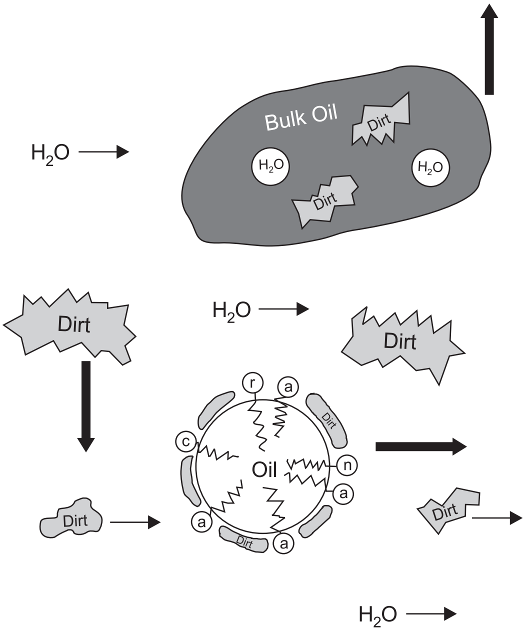


Figure 27.8 Action taking place in API and CPI separators.

There are two basic methods of air flotation in use: DAF and IAF. DAF uses water under pressure, which becomes supersaturated in air upon release of the pressure. Bubbles of 30–120 μm are released and promote flotation. In areas where risk of explosion is present, dissolved nitrogen flotation (DNF) is used. Nitrogen flotation is not as efficient as air flotation due to solubility differences between pure

	Typical Effluent Concentration, mg/L			
Process	**BOD$_5$***	**COD†**	**TSS‡**	**Oil**
API separator	250–350	260–700	50–210	20–100
CPI separator				20–100
	Typical Removal Efficiency, %			
API separator	5–40	5–30	10–50	60–99
CPI separator				60–99

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*Biochemical oxygen demand after five days.

†Chemical oxygen demand.

‡Total suspended solids.

Table 27.1 Expected Effluent Results and Removal Efficiency Using Gravity Separation on Refinery Effluent nitrogen and air. IAF utilizes mechanical agitation with air either aspirated or pumped into the mixing area. Larger air bubbles, typically 0.5 to 1 mm in size, promote flotation.

Dissolved Air Flotation DAF is used extensively, particularly in the refining industry. Table 27.2 lists the three basic modes of DAF and shows advantages and disadvantages of each.

DAF functions by altering particulate density through incorporation of air onto or into the floc structure. Bubbles become attached by:

- Adhesion of bubble to particle by collision, or as a condensation site
- Entrapment of bubble in floc structure
- Adsorption of bubble in floc structure

An illustration of oily sludge being formed is presented in Fig. 27.9. Air bubbles are formed in and around suspended solids and emulsified oil droplets. As droplets coalesce, air is trapped within and on the floc structure, producing floc less dense than water. Eventually, the floc becomes a continuous oily sludge.

The DAF system typically includes the following hardware:

- DAF float tank (circular or rectangular)
- Air saturation system
- DAF recycle pump (for recycle pressurization system)
- Air compressor or source of high-pressure air
- Rapid mix or flocculator tanks that are either separate or part of the DAF unit

System	Advantages	Disadvantages
Full pressurization	More gas/hour dissolved, higher separation efficiency.	Must pump influent solids, can emulsify oil in influent, high power requirements.
Partial pressurization	Lower power required compared to full pressurization.	Less gas/hour dissolved, must pump influent solids, can emulsify oil in influent.
Recycle pressurization	Do not need to pump influent solids, optimizes floc formation, influent oil not emulsified, simpler control.	Requires larger flotation cell.

Table 27.2 Comparison of DAF Pressurization Methods

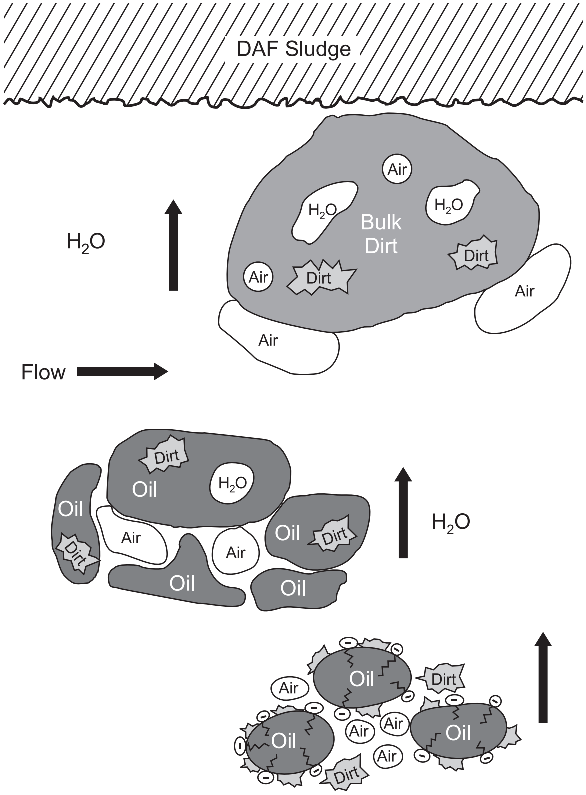

FIGURE 27.9 DAF sludge.

The air saturation system can be described as the heart of the DAF process (Fig. 27.10). In a recycle pressurization system, air is dissolved in the recycle water flow under pressure. This occurs in the air saturation tank, which should be about 50% full of recycle water.

When evaluating DAF units, the most important operational criteria is hydraulic loading, expressed as gpm/ft^2 (m^3/[h·m^2]) of DAF surface area, and detention time. The hydraulic loading rate is calculated as follows:

$$\text{HLR} = \frac{I + R}{A} \tag{27.1}$$

where HLR = hydraulic loading rate, gpm/ft^2 (m^3/[h·m^2])
I = influent flow rate, gpm (m^3/h)
R = recirculation flow rate, gpm (m^3/h)
A = DAF surface area, ft^2 (m^2)

Figure 27.10 The float produced by DAF of an oily effluent (o/w) emulsion. (*Courtesy of Infilco Degremont Inc.*)

Typical hydraulic loading rates range from 1 to 2 gpm/ft^2 (2.4–4.9 m^3/[h · m^2]), depending on equipment manufacturer. Hydraulic loading for the average flow condition should be about 1.5 gpm/ft^2 (3.7 m^3/[h · m^2]).

Detention time is calculated as follows:

$$\mathrm{DT} = \frac{V}{I + R} \tag{27.2}$$

where DT = theoretical hydraulic detention time, min (h)
V = tank volume, gal (m^3)
R = recirculation flow rate, gpm (m^3/h)
I = influent flow rate, gpm (m^3/h)

Hydraulic loading and detention time can be checked and compared to design values to determine if the unit is hydraulically overloaded.

DAF performance should be judged on the following factors:

- Effluent quality
- Oil removal efficiency
- Improving throughput or capacity
- Polymer dosage required

Process	Typical Removal Efficiency, %			
	BOD_5	COD	TSS	Oil
DAF treatment	25–70	10–60	50–85	70–85

TABLE 27.3 Typical DAF Removal Efficiency

Removal efficiency can be determined using Eq. (27.3):

$$R = \frac{100(I_c - E_c)}{I_c} \tag{27.3}$$

where R = removal efficiency, %
I_c = influent oil concentration, mg/L
E_c = effluent oil concentration, mg/L

Table 27.3 shows typical removal efficiency for DAF units.

For oily waste treatment, skimmings should not be allowed to become more than 2 inches (51 mm) thick, since turbulence might re-emulsify the oil. Skimmers are frequently run constantly to keep oil layers from building up. Skimmer speed and submerged depth may be adjusted to improve formation and removal of oil skimmings. If turbidity levels in subnatant from the unit are rising, increasing skimmer speed to remove skimmings more quickly can help.

Induced Air Flotation IAF units were originally developed for removing fine particles from mineral slurries and concentrating mined material. However, the units found other uses, notably in oilfields for separating oil from water. IAF is used in effluent treatment of oily wastes at refineries, steel mills, railroad yards, shops, and other miscellaneous industries where oils are a problem in waste streams, where the oil more readily separates from water. These units are often used in place of DAF units, since IAF units can be operated at much higher hydraulic loadings (higher flow throughput for equivalent surface area). Therefore, the capital cost for treatment equipment is lower. IAF differs from DAF as shown in Table 27.4.

In general, a DAF unit can be characterized as a quiescent, high retention time device using relatively small quantities of dissolved air, while IAF is a low retention time, less quiescent machine using a relatively large quantity of air. Froth flotation in the IAF is usually enhanced by chemical treatment. Chemical dosage can range from 5 to 15 mg/L in IAF units, but is dependent on loading and oil characteristics.

IAF units consist of a headbox for even distribution of influent flow, four flotation cells in series with skimmer paddles on each side, equipment to induce or disperse air into the waste flow, an effluent box, and a level control mechanism on the discharge pipe or in the effluent box.

Induced (Dispersed) Air Flotation	Dissolved Air Flotation
Air is mixed with liquid, not dissolved.	Air is dissolved in liquid. Air saturation equipment is required.
Surface interaction between air bubble and oil or solids provides basis for separation.	Flotation of impurities (solids and oil) due to air attachment to solids or oil.
Air bubble size is larger (>100 μm).	Air bubble size is smaller (10–100 μm).
Kinetics of IAF is rapid. Relatively short detention times (loading rates are higher).	Lower loading rates and therefore longer detention times and slower particle rise rates.
Energy and shear turbulence are generally greater.	Turbulence below or at surface should be minimal in well-designed and operated system.
Chemicals are added to cause oil and suspended solids to engulf air bubbles and be floated to the surface.	Chemicals are added to flocculate oil (or break emulsion) and suspended solids to form larger floc so bubbles have greater floc area for attachment.
Clarification only (oil and solids removal).	Clarification and sludge thickening (typically for secondary sludge at municipalities and paper mills).

Table 27.4 Induced versus DAF

Two methods are used to induce air into the waste flow:

- Impeller type device where each cell is equipped with a turbine motor (Fig. 27.11)
- Nozzle air recycle flow flotation unit (Fig. 27.12)

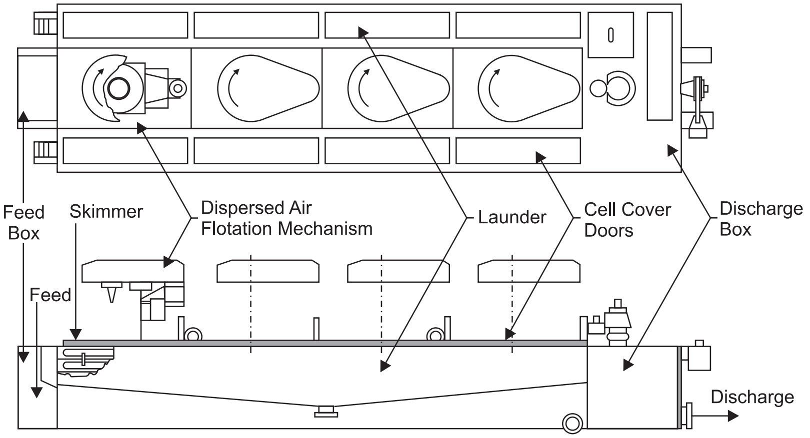

Figure 27.11 Impellor-type IAF unit.

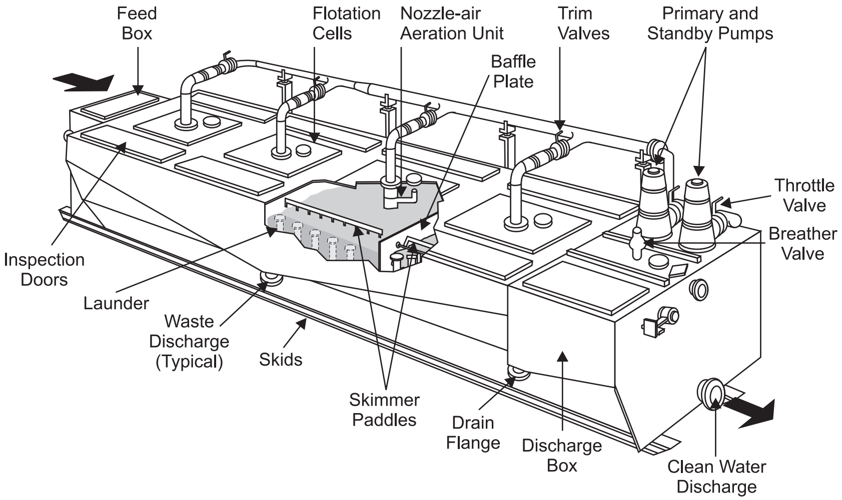

Figure 27.12 Nozzle air aeration IAF unit. (*Courtesy of Wemco Division, Envirotech Corporation*.)

The impeller unit consists of a star rotor suspended between a cylindrical standpipe and draft tube. Rotation of the rotor generates a liquid vortex pattern with an air–liquid interface extending from the midpoint of the inner wall of the standpipe, through the interior of the rotor section down to the upper section of the draft tube (Fig. 27.13). This air cavity formed within the vortex serves to

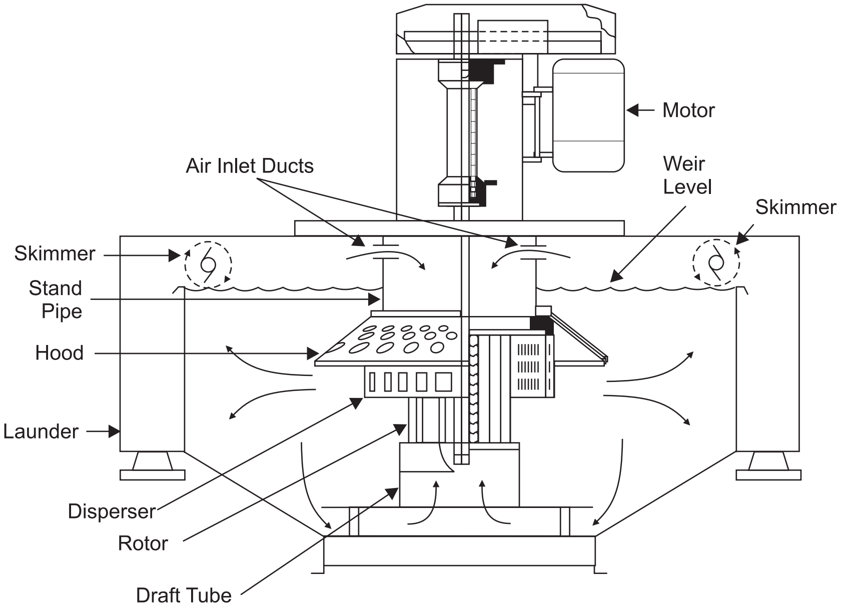

Figure 27.13 IAF impellor detail.

induce air from the freeboard of the vessel, through air inlet ducts into the interior of the rotor. Impeller rotation causes liquid to circulate upward from the bottom of the vessel through the draft tube to the rotor, where it mixes with air. This produces an air–water mixture that leaves the impeller section tangentially. By passing the air–water mixture through holes of a disperser that surrounds the impeller, the direction of flow is changed to radial. Contaminant-laden air bubbles then separate by gravity and rise to the liquid surface. The separation region is maintained in a relatively quiescent condition.

Nozzle air flotation units are mechanically simpler than the impeller. Air injection is accomplished hydraulically by recycling a portion of relatively clear liquid effluent to each of the four cells in the unit. As pressurized flow passes by a nozzle opening, air is drawn into the recycle flow by the pressure differential between the ambient air and recycles flow. Manual valves are located on the recycle line to each cell to control or adjust the amount of recycle and air induced into each cell (see Fig. 27.14).

Membrane Filtration

For oily effluent treatment, tubular UF membranes are commonly used. Highly hydrophilic membranes are used in these systems to allow water to pass through and hydrophobic oils to be retained by the membrane. Free oil is usually removed before sending effluent to the membrane system to avoid membrane fouling. Oily effluent is concentrated by UF, significantly reducing its volume.

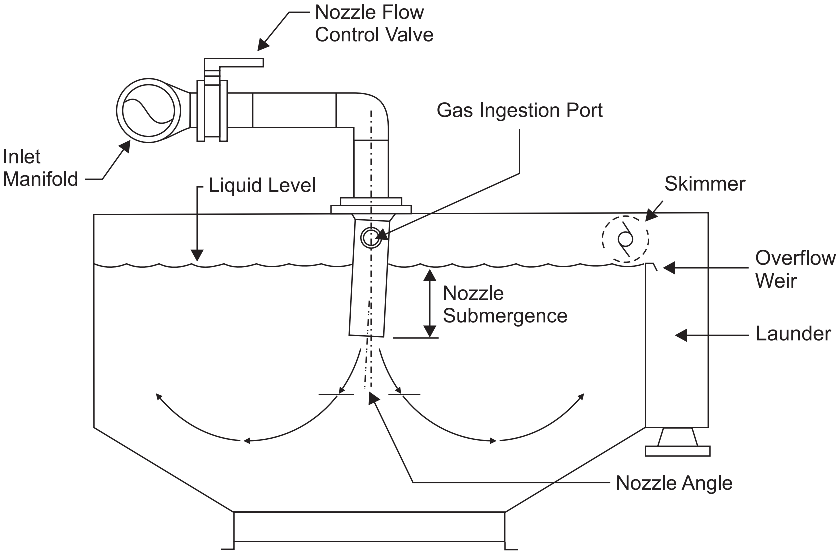

Figure 27.14 IAF nozzle air cell detail.

Water-in-Oil Emulsions

Waste oil (w/o) treatment involves recovering oil from an emulsion, using one or more of three common treatment methods: treatment by transfer, pH adjustment, and internal mixing. Each method includes chemical treatment.

Batch processing of the emulsion is common to all three methods. Application of heat and chemicals during processing is common to all three treatment methods as well.

Treatment by Transfer

The most common method of oil recovery is a batch treatment process, commonly requiring several tanks. Typically, oil skimmings are pumped to one or two holding tanks. Batch treatment is generally limited to 3000 barrels (480 m^3) or less, to permit transfer of the batch in one day. Larger batches tend to suffer from poor mixing and require longer resolution times.

Before any chemical treatment is applied, slop oil is preheated to 150 to 180°F (66–82°C) by means of steam coils in the slop oil holding tank, or a heat exchanger in the transfer line. Heating allows for better mixing of treatment chemicals, lowers viscosity of the emulsion, and speeds up resolution of the emulsion. Without heating, the emulsion may not resolve at all or may need several thousand mg/L of chemical.

Emulsion breaking chemical is added to the slop oil, while it is transferred from the holding tank to the batch treatment tank (see Fig. 27.15). Batch treatment in one tank is possible using recirculation, as long as the temperature is maintained below 180°F (82°C). Once treatment chemical has been added, the recirculation agitation is turned off, and the emulsion is allowed to separate. Often, there is an oil-wet layer of solids that still contains water called the "rag layer." Recirculation does not ensure proper distribution of chemical,

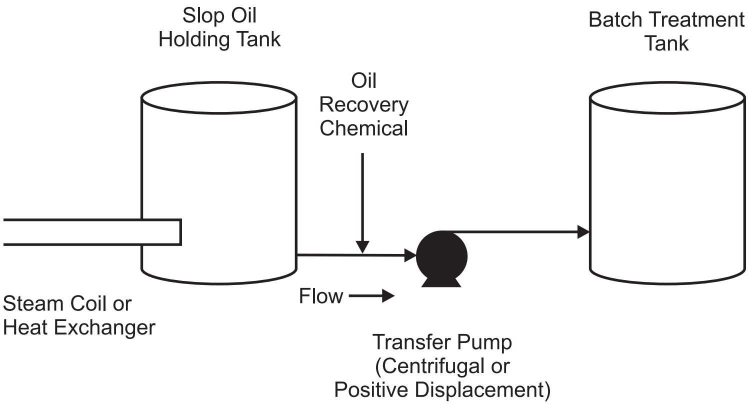

FIGURE 27.15 Typical oil recovery scheme for treatment by transfer.

and dosage consistency is better achieved by feeding chemical at the required dosage in proportion to the slop oil transfer rate. For example, if the dosage needed is 3000 mg/L (volumetric dosing), and the transfer rate is 100 bbl/h (16 m^3/h), then the chemical feed pump should be calibrated to deliver 12.6 gph (47.7 L/h) or 0.21 gpm (0.8 L/min). Failure to feed proportionately can result in poor resolution.

$$\begin{aligned} \text{FR} &= \frac{(3000\ \text{mg/L})(100\ \text{bbl/h})(42\ \text{gal/bbl})}{10^6} \\ &= 12.6\ \text{gph or } 0.21\ \text{gpm} \end{aligned} \tag{27.4a}$$

or

$$\begin{aligned} \text{FR} &= \frac{(3000\ \text{mg/L})(100\ \text{bbl/h})(159\ \text{L/bbl})}{10^6} \\ &= 47.7\ \text{L/h or } 0.8\ \text{L/min} \end{aligned} \tag{27.4b}$$

The treated slop oil emulsion should enter the batch tank at or near the bottom to enhance formation of the free oil layer. Pumping into the top of the tank tends to disrupt and re-emulsify the free oil layer. This can result in a longer resolution time or poor oil recovery.

When the transfer is completed, treated slop oil is allowed to stand for as long as possible, usually 12 to 48 hours. It is not normally necessary to maintain temperature during the resolution period. The emulsion resolves as the tank cools. Shortening the settling time can cause poor oil recovery or poor oil quality.

pH Adjustment

Another approach in waste oil emulsion breaking for oil recovery is pH adjustment. The pH has a significant effect on stability of the emulsion. Lowering pH provides hydrogen (H^+) ions for neutralization of negative charges surrounding water in w/o emulsions.

As with treatment by transfer, slop oil is preheated to 150 to 180°F (66–82°C) by means of steam coils in the slop oil holding tank or a heat exchanger in the transfer line. Heating allows for better mixing of treatment chemicals, lowers viscosity of the emulsion, and speeds up resolution of the emulsion. Without heating, the emulsion may not resolve at all or may need several thousand mg/L of chemical. The traditional method is to lower pH to the 2 to 4 range to increase emulsion breaking efficiency. During bench testing, the effect of pH should always be investigated, both increasing and decreasing the pH level.

Treatment by Internal Mixing

All sludge treatment programs require some heating to usually 180°F (82°C) with thorough agitation in a vessel commonly called a cooking vessel (see Fig. 27.16). Since bubbles of steam collapse immediately and cool quickly, the cooker may vibrate and make noise, but there is little significant motion to the sludge itself. Temperatures greater

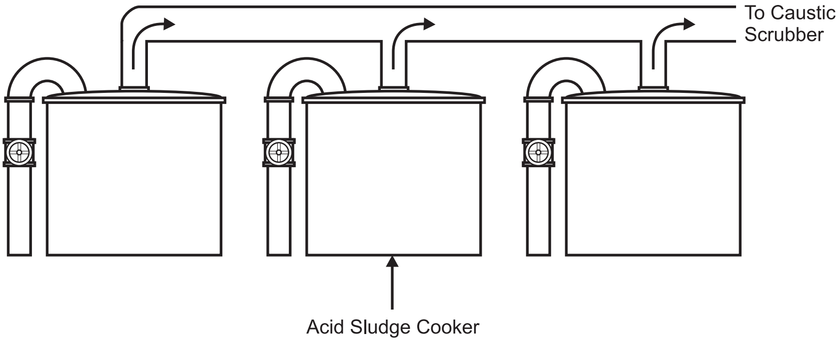

Figure 27.16 Acid sludge cookers (vents lead to caustic scrubbers).

than 180°F (82°C) should be avoided when cooking DAF sludge, as it may cause foaming and exceed the vessel volume.

Mechanical agitators, such as turbine mixers, work well in cases where the cooker is heated mainly with steam coils or plates. The shaft of the mixer should extend about 2/3 of the working depth into the cooker. Some baffling in the cooker may be needed to achieve proper rolling action. Baffling may be accomplished by hanging plates, coils, or pipes in the cooker.

Foaming may occur during addition of acid. Therefore, concentrated sulfuric acid should be added to a cooker before the temperature reaches 140°F (60°C).

Once the cooker has reached the desired temperature and chemicals have been added, agitation is stopped, and the emulsion is allowed to separate.

Lowering pH to break the emulsion is deemed a last resort method. Low pH with high temperatures causes significant corrosion damage to mild steel tanks, pipes, and pumps.

Water-in-Oil Emulsion Processing

Once waste oil has been treated, it can be separated into water and oil by gravity separation in a tank or processing through either a 2-phase or 3-phase centrifuge. Allowing waste oil to separate in a tank often produces a rag layer (oil wet solids and water), which is often difficult to manage because the oil-wet solids have a tendency to form an emulsion at the oil–water interface.

Processing by centrifuge allows separation of liquid from the solids, and then oil is separated from the water. In a 2-phase centrifuge, liquid and solids are separated, and the liquid (oil and water) then goes to a separation tank to allow for oil–water separation. A 3-phase centrifuge separates solids from the liquid phase, but at the liquid exit port on the centrifuge, a weir separates oil from water. Thus, no separate settling tank is required.

CHAPTER 28

Wet Gas Scrubbers

Wet scrubbers use a liquid to remove solid, liquid, or gaseous contaminants from a gas stream. The scrubbing liquid performs this separation by dissolving, trapping, or chemically reacting with the contaminant.

Scrubbers are used extensively to control air-polluting emissions. So many different scrubber configurations have been used that there is some confusion as to whether they all belong in the same category. In some references, for example, the definition of a scrubber may be restricted to certain design criteria, such as whether the units are open or packed. In this text, any device fitting the definition of the first sentence is a wet scrubber.

Scrubber systems can be designed to remove entrained particulate materials such as dust, fly ash, and metal oxides, or to remove gases such as oxides of sulfur (SO_x) from a flue gas stream to meet air emission standards.

Particle Collection Concepts

In scrubbing particulate matter from gases, the principal concern is usually removal of particles smaller than 10 μm. Larger particles are relatively easy to separate. Successful design and operation of wet scrubbers depend on knowing the size, composition, and derivation of particles to be collected.

Figure 28.1 shows the estimated size for some common pollutants. Just as fine particles in water (colloids) carry a charge of static electricity, so do colloidal particles in fumes and dust, defined as aerosols. If these particles carry no charge, they may be deliberately charged to assist removal in electrostatic precipitators.

Among particulates (term for suspended solid materials) collected by wet scrubbers are dispersion aerosols from processes such as grinding, solid and liquid atomization, and transport of suspended powders by air currents or vibration. Dispersion aerosols are usually

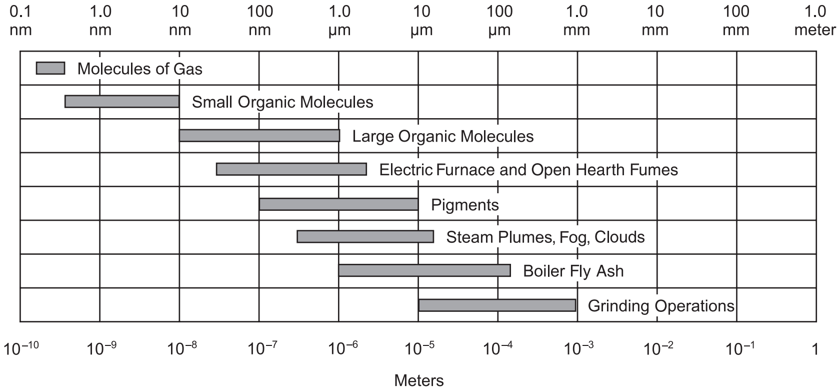

FIGURE 28.1 Comparison of particle sizes in air emissions.

coarse and contain a wide range of particle sizes. Dispersion aerosols consisting of individual or slightly aggregated, irregularly formed particles, are called dusts.

Condensation aerosols are formed when supersaturated vapors condense, or when gases react chemically, forming a nonvolatile product. These aerosols are usually smaller than 1 µm. In condensed aerosols, solid particles are often loose aggregates of a large number of primary particles of crystalline or spherical form. Condensation aerosols with a solid dispersed phase, or a solid–liquid dispersion phase, are classed as smokes or fumes. Aerosols that include a liquid dispersion phase are called mists. This classification usually applies regardless of particle size, and differentiation is sometimes difficult.

In practice, combinations of dispersion and condensation aerosols are encountered. Different size particles behave differently because of physical properties such as light scattering, evaporation rates, and particle movement. The choice of the best device for particle removal from gas is affected by these differences. Microscopic sizing and density estimation may obtain particle sizes, volumes, and weights.

Particulate Emissions

Limits on particulate emissions (smoke, mist, dust) are usually established in four ways:

1. Emission rate: Maximum weight that can be legally emitted in pounds (kilograms) per hour. This may be expressed as the rate for a specific industry in production terms, for example, pounds per hour per ton (kilograms per hour per tonne) of pulp.

2. Maximum concentration: Maximum amount of particulate matter in the gas stream released, for example, g/m^3, grains/ft^3, or lb/1000 lb gas.
3. Maximum opacity: Maximum opacity of the gas stream emitted, usually measured by observation and comparison to empirical standards (Ringlemann numbers).
4. Corrected emission rate: This is tied to an air quality standard by a formula based on atmospheric dispersion considerations.

Often, several particular emission regulations are enforced simultaneously. If all four types of restrictions are employed, a plant might pass on emission rate and concentration, but fail on opacity. This is an understandable situation, since large particles are major contributors to weight, while smaller particles in the 0.1 to 2.0 μm range are major contributors to opacity.

Addition of chemical additives to scrubber water to capture particles in the 0.1 to 2.0 μm range is often an economical way to meet air quality standards, particularly when compared to the cost of process modifications and equipment additions.

Wet scrubbers discussed in this chapter use water to remove particulates, gases, or both from industrial gas streams or stacks. Water chemistry is often extremely complicated in these scrubber systems, because of the variety of operations occurring simultaneously in the scrubber environment, such as;

Heat transfer: The gas and water are often at different temperatures, and heat is transferred in the scrubbing process.

Evaporation/condensation: The gas may be hot and saturated with water vapor. Contact with colder water dehumidifies the gas, and scrubbing water is diluted with condensate. If stack gas is hot and dry, scrubber water evaporates as in a cooling tower and becomes concentrated.

Mass transfer: The gas may contain water-soluble solids or gases that dissolve in scrubber water. Water may transfer gases to the gas stream as well. For example, water may be recycled over a cooling tower becoming saturated with oxygen (O_2) and nitrogen (N_2), later releasing them to the gas stream.

Scaling: As scrubber water is heated or increases in pH, alkalinity, or sulfate–sulfite content, precipitation of calcium carbonate ($CaCO_3$), calcium sulfate ($CaSO_4$), or calcium sulfite ($CaSO_3$) may occur, and the scrubber may become scaled.

Corrosion: A common and troublesome problem encountered in most wet scrubbers.

Fouling: Fouling may occur from coagulation of the particulate being removed or from microbial activity. Many industrial gas streams contain organics that supply food to microbes.

Principles of Operation

Scrubber manufacturers offer a bewildering array of products. Scrubbers are available in a wide range of designs, sizes, and performance capabilities. Some are designed primarily for collection of particles and others for mass transfer (gas removal by a chemical reaction). As good liquid–gas contact is needed for both operations, all scrubbers can collect both particles and gases to some extent. The degree to which particle collection and mass transfer characteristics of a scrubber can be utilized, determines applicability of the scrubber for each specific purification problem. Figure 28.2 shows the commonly accepted domain of wet scrubbers based on particle size, relative to other competitive devices. Figure 28.3 shows relative particulate removal efficiency of the more common types.

Particle size is one of the most important factors affecting removal efficiency, larger particles being much more easily removed. Submicron particles are the most difficult to remove.

All wet particle scrubbers operate on the same basic aerodynamic principle. A simple analogy: If water droplets of basketball size were projected to collide with gas-stream particles the size of bee bees (BB), statistical chances of collision are small. As the size of the water droplets is reduced to more nearly the size of the particles, chances of collision improve. Studies have shown that a surface film surrounding a water droplet has an approximate thickness of 1/200 of its diameter. A BB (the particle in flight) having a diameter less than 1/200 the diameter of the basketball flows through the streamline film around the basketball without collision (Fig. 28.4). However, if the water droplet were a baseball instead of basketball, collision would occur. A 0.5 µm fume particle requires water droplets smaller than 100 µm for adequate collection. Efficient scrubbing, therefore, requires atomizing the liquid to a fineness that is related to particle size, to afford maximum contact with the particles to be captured.

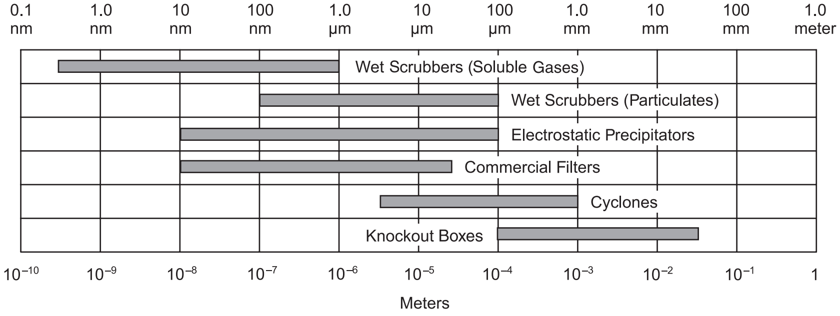

FIGURE 28.2 Application of wet scrubbers compared to competitive devices.

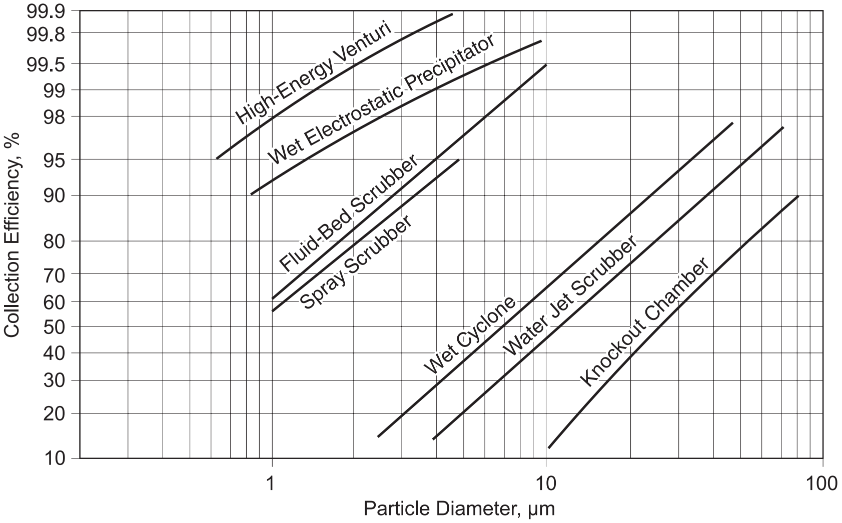

FIGURE 28.3 Performance range of scrubbing devices.

The probability of a droplet hitting the dust particles is proportional to the dust concentration; a ball would be less likely to hit a single BB than a swarm of them. To equalize these factors, scrubbers are regulated as to the volume of gas to be scrubbed (measured by pressure drop of gas stream) and water to be sprayed (measured by hydraulic pressure at the spray nozzles). Scrubbing chamber height and diameter are also tailored to the known characteristics of the gas.

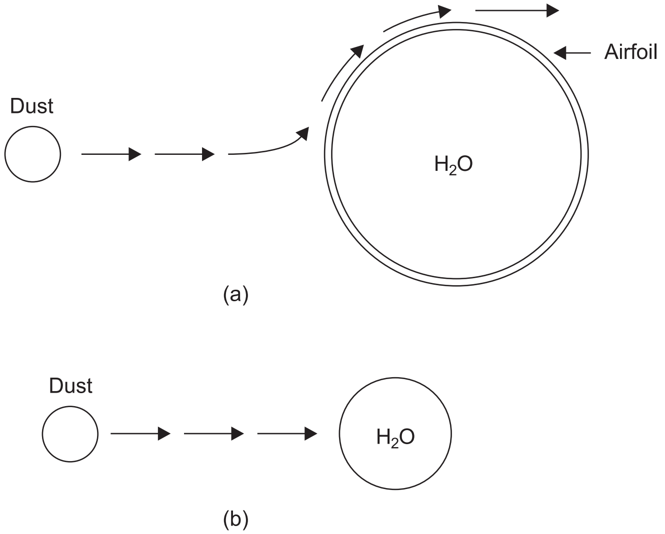

FIGURE 28.4 Effect of relative water droplet size to particle size for capture.

Categorizing Wet Scrubbers

Wet scrubbers differ principally in their methods of effecting contact between the circulating liquid and gas stream. Techniques employed include injecting liquid into collection chambers as a spray, flowing liquid into chambers over weirs, bubbling gas through trays or beds containing liquid, and atomization of liquid by injection into a rapidly moving gas stream.

One way of categorizing wet scrubbers is by energy requirements. Some require high energy while others require very little. Generally, low-energy scrubbers are used for removal of large particulate matter and gaseous contaminants. They rely on high liquid/gas ratios and contact time in the scrubber to increase removal efficiency. High-energy scrubbers are used for removal of very small particulates (1 μm and less). They depend on high gas velocity for atomization to form small liquid droplets, with maximum impact between water droplets and particulate matter.

A second way of categorizing wet scrubbers is based on selectivity toward either gaseous contaminants or particulate matter. Scrubbers designed primarily for removal of gas are called mass transfer scrubbers or gas absorbers; those designed for removal of particulate are called wet particle scrubbers.

Gas Absorption Scrubbers

Gas absorbers are designed to maximize contact time and surface area between the scrubbing liquid and gas. This provides maximum opportunity for liquid–gas chemical reactions to occur. Absorption scrubbers usually have low energy requirements. Types most commonly used are packed bed, moving bed, plate, and impingement scrubbers. Although wet particle scrubbers provide mass transfer removal of some gases, these four types of absorption scrubbers do the job more completely and with greater efficiency.

Mass transfer (gas absorption) reactions require long residence times because contaminants must first be absorbed by scrubbing liquor and then react chemically to form a product that remains in the liquid phase.

Packed Tower

The packed tower (packed bed) consists of a vertical vessel containing packing materials such as rings, saddles, or tellerettes (Fig. 28.5). Water is sprayed across the top of the bed and trickles through the packing material. Gas enters near the bottom, and contaminants are removed as the gas stream moves upward through the water-washed packing.

The cleaned gas stream passes through a mist eliminator near the top, where entrained moisture is removed before discharge. Scrubbing

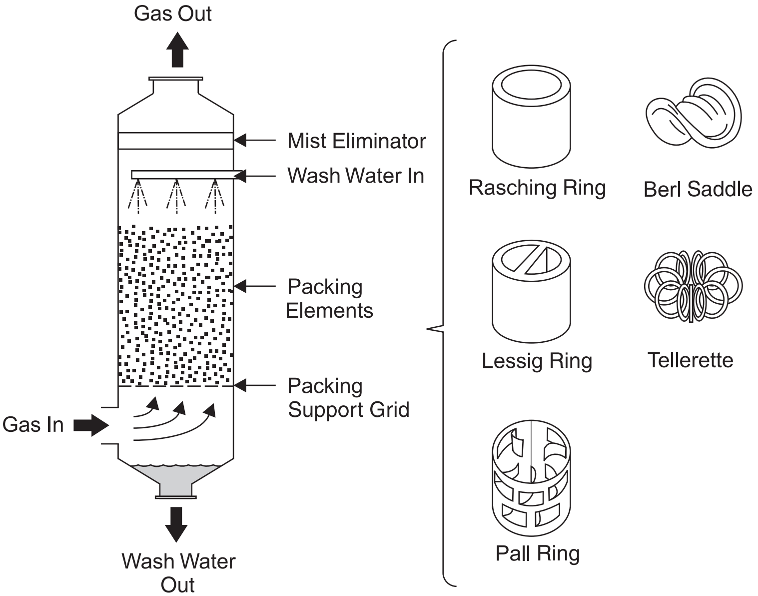

FIGURE 28.5 Packed tower and types of packing.

liquor is collected at the bottom. A portion is usually recycled to the inlet, and the balance discarded.

Although flows can also be co-current or crosscurrent, the countercurrent type is most widely used. Packed beds have long been used for gas absorption operations, because they are able to reduce odor and pollutant gases to low residual concentrations. The limiting factor is economics. As better separation is needed, beds require greater packing depth and operate with higher pressure drops.

Gases entering a packed bed should not be heavily laden with solid particles, as these cause clogging of the packing material. Pressure drop is typically 0.5 inches of H_2O per foot of packing (3 mm Hg/m).

Typical applications include rendering plants, food processing plants, sewage treatment plants, and metal pickling plants.

Moving Bed Scrubbers

Moving bed wet scrubbers are well suited for high heat and mass transfer rates (Fig. 28.6). They are able to handle viscous liquids and heavy slurries without plugging. They accomplish this by using lightweight sphere packing that is free to move between upper and lower retaining grids. Counter-current gas and liquid flows cause the spheres to move in a random, turbulent motion, creating intimate mixing of liquid and gas. In addition to excellent gas–liquid contact, turbulence provides continuous cleaning of the moving spheres to minimize plugging or channeling of the bed.

Figure 28.6 Moving bed scrubber using lightweight packing of spheres that continually shift, preventing plugging. (*Courtesy of The Ducon Company, Inc.*)

Moving bed scrubbers are useful for absorbing gas and removing particulates simultaneously. This type of scrubber is especially suited for use with gases containing viscous or gummy substances, which would result in plugging of conventional packed bed scrubbers. Efficiency is good for collection of particles larger than 1 μm. Both particle collection and gas absorption efficiency may be increased by employing several stages in series. Pressure drop is typically 0.2 to 0.5 inches H_2O (0.37–0.93 mm Hg) per stage.

Turbulent Contact Absorber The turbulent contact (TCA) absorber was developed as an extension of the moving bed scrubber, the difference being increased turbulence in the TCA unit, resulting from using fewer spheres per unit volume. The TCA enhances beneficial characteristics of the moving bed scrubber and permits high liquid and gas flows.

Plate Scrubbers

A plate scrubber consists of a tower having plates (trays) mounted inside (Fig. 28.7). Liquid introduced at the top flows successively across each plate as it moves downward. Gas passing upward through the openings in each plate mixes with liquid flowing over it. The gas–liquid contact causes gas absorption or particle removal.

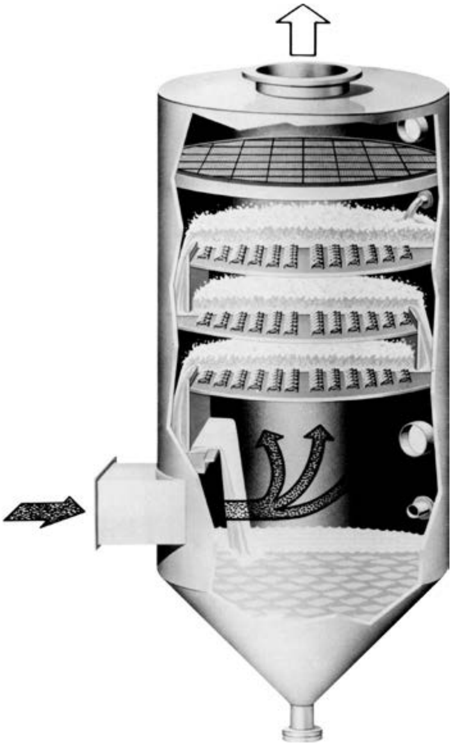

FIGURE 28.7 Plate scrubbers provide intimate gas–liquid contact. Flat plates are kept free of deposits in most applications by turbulence. (*Courtesy of Koch Engineering Company, Inc.*)

A plate scrubber is named for the type of plates it contains; if the plates are sieves, it is called a sieve plate scrubber.

Impingement Scrubbers

In some designs, impingement baffles are placed a short distance above each perforation on a sieve plate forming an impingement plate, to increase turbulence and enhance gas-particle–liquid interaction (Fig. 28.8). Impingement baffles are below the liquid level. Pressure drop is about 1 to 2 inches H_2O (1.9–3.7 mm Hg) for each plate.

Wet Particle Scrubbers

The four basic factors that determine the efficiency of wet particle scrubbers are:

1. Water surface area
2. Liquid/gas ratio
3. Particle size and scrubber energy
4. Particulate affinity for water (wettability)

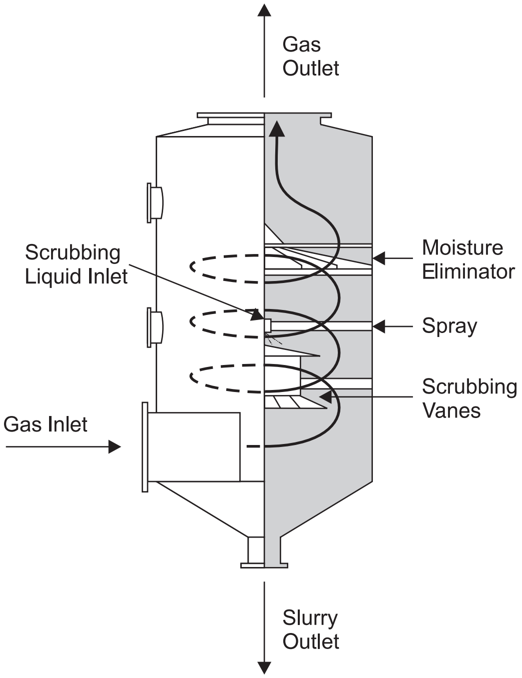

Figure 28.8 An impingement scrubber uses a perforated plate to promote gas–liquid contact with impingement baffles over the perforations to atomize water. (*Courtesy of W.W. Sly Manufacturing Company*.)

Anything mechanical or chemical that causes water spray nozzles to form smaller water droplets with larger surface area increases the collision rate between particulate in the gas phase and water, resulting in increased particulate removal.

The second way to increase the collision rate is to pump more water through the scrubber. However, increasing the liquid/gas ratio is an inefficient means of increasing the surface area of water. Usually, it is more economical to increase the effective liquid/gas ratio by causing smaller droplets to form mechanically or chemically.

The force, with which particulate matter strikes water, is a third factor in scrubber performance. Since a liquid film barrier separates particulate in the gas phase from water, a particle must have enough energy to force its way into the water droplet to be captured. Smaller particles require more energy than larger ones. They have a lower mass, and strike the barrier with less momentum than larger particles moving at the same velocity. Therefore, higher energy is required for scrubbing small particles than for large particles.

Higher energy must be expended to scrub a particle that is hydrophobic (repelled by water) than a similar size particle that is hydrophilic (attracted to water), and most particulates in the gas stream are hydrophobic. Increasing the mechanical energy of a wet scrubber increases its ability to remove smaller and more hydrophobic particulates.

Another means for increasing removal of these particles is increasing the wetting power of water by chemical reduction of surface tension.

Either a high-energy or a low-energy scrubber may be used for removal of particulates from gas streams, the choice depending on size of the particles. Low-energy scrubbers, such as the spray tower and wet cyclone, may be used for particles over 5 μm. For particles smaller than 5 μm, a high-energy scrubber such as a venturi or a venturi ejector provides more complete removal. Many wet scrubbing systems, such as those cleaning steel mill blast furnace gases, employ a low-energy scrubber followed by a high-energy scrubber. The function of the low-energy scrubber is to cool the gas (reduce volume) and remove large particles, thereby reducing load on the high-energy venturi scrubber. This also reduces size and power of the induced draft fan, because the cooling effect reduces gas volume.

Spray Towers

The spray tower collects particles or gases on liquid droplets produced by spray nozzle atomization. Characteristics of droplets are determined by nozzle design. Sprays are directed into a chamber shaped to conduct gas to the atomized droplets. Spray towers can be used for both mass transfer and particle collection. Low-pressure drop [1–2 inches H_2O (1.9–3.7 mm Hg)] and high water rate make them the least expensive of the mass transfer scrubbers. Spray towers are most applicable for removal of large particles, gas cooling, humidification, dehumidification, and removal of gases with high liquid solubility.

Wet Cyclones

Wet cyclone scrubbers (Fig. 28.9) are effective for removing dusts and liquid aerosols. Finely atomized water spray, contacts the gas stream, which enters tangentially at the bottom to pursue a spiral path upward. Atomized droplets are caught in the spinning gas stream and swept by centrifugal force across to the walls of the cylinder, colliding with, absorbing, and collecting dust or fume particles en route. Scrubbing liquid and particles drain down the wall to the bottom, and clean gas leaves through the top. The higher pressure drop [6–8 inches H_2O (11–15 mm Hg)] increases energy costs over those for a spray tower.

Venturi Scrubbers

Venturi scrubbers (Fig. 28.10) are best suited for removal of 0.05 to 5 μm particulates, such as those created by condensation of a liquid,

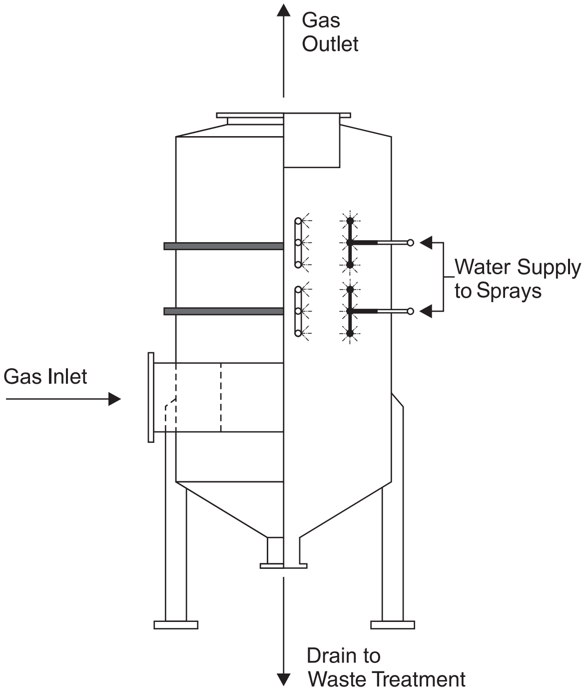

FIGURE 28.9 Wet cyclone scrubber. (*Courtesy of Ceilcote Company, a unit of General Signal*.)

metallic vapor, or by a chemical reaction forming a mist or fume. Typical examples are ammonium chloride fumes from steel galvanizing, phosphorus pentoxide fumes from phosphoric acid concentration, mists from dry ice plants, and zinc oxide fumes from reverberatory furnaces.

Passing gas and water streams co-currently through the extremely small throat section of a venturi remove aerosols. As the velocity is accelerated in the throat, the liquid breaks into extremely fine drops. High gas velocities, ranging from 200 to 400 ft/s (61–122 m/s), make the relative velocity between gas and liquid high enough to cause good liquid atomization and particle collection. Liquid drops collide with and remove particles in the gas stream, and then agglomerate for separation from the gas. The cleaned gas stream passes through a separator to eliminate entrained liquid.

Venturi scrubbers require high pressure drops [5–100 inches H_2O (9.3–187 mm Hg)]. Pressure drop must be increased as particle size becomes smaller to ensure adequate removal.

Venturi scrubbers can be used for removing soluble gases. However, such applications are limited to situations where small particulates are also present, since high-energy requirements for

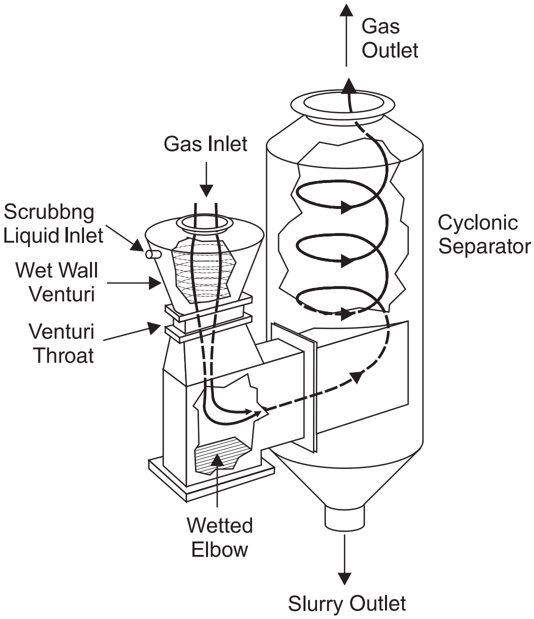

FIGURE 28.10 Venturi scrubber with variable throat to accommodate changes in gas flow. (*Courtesy of FMC Corporation*.)

operating venturi scrubbers make them costly for controlling gaseous pollutants.

Several modifications of the basic venturi scrubber are available to meet specific requirements of the size and type of particle to be removed. Low, medium, or high-energy venturi scrubbers are available, with energy requirements directly related to the pressure drop needed for removal of submicron particulates.

Many venturi scrubbers have a variable throat to allow for change in load. In addition, as the throat is decreased in size at a fixed load, velocity increases, resulting in increased pressure drop and better efficiency in removing submicron particles.

Venturi scrubbers use several methods to atomize scrubbing water. In the most common, liquid is sprayed through jets across the venturi throat (Fig. 28.10). This provides effective removal of submicron dust, fume, and mist particles and is the first choice for the majority of applications. In another common venturi, the flooded wall type, scrubbing liquid is introduced tangentially at the top, as shown in Fig. 28.11. Liquid spirals down converging walls to the throat in a continuous film. At the entrance of the throat, it forms a curtain of liquid in the gas stream. Impaction of gas into this curtain atomizes the liquid. Further impaction and agglomeration occur in the diverging section.

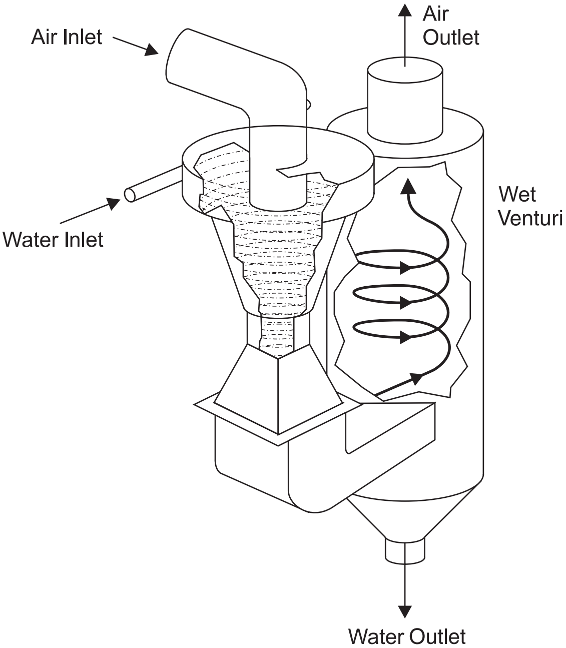

Figure 28.11 In this venturi scrubber design, water is atomized and flows down a spiral path toward the venturi throat.

This type of venturi scrubber is recommended for hard-to-handle situations like removal of sticky solids from gases, recycling of dirty water where water supplies are limited, and recovery of process materials in concentrated form.

Another common type is the flooded disk scrubber, in which liquid is introduced to a disk upstream of the venturi throat. Liquid flows to the edge of the disk and is atomized by the high-velocity gas stream.

Figure 28.12 shows an ejector venturi, which uses high-pressure spray nozzles to collect particulates, absorb gases, and move the gas. It derives its energy from high-pressure liquid, while the regular venturi derives most of its energy from high gas velocity produced by the induced draft fan. Depending on the ejector venturi used, an induced draft fan may or may not be required.

There is a high velocity difference between the liquid droplets and gas; this affects particle separation. Collection efficiency is generally high for solid particles larger than 1 μm. Mass transfer is affected by the co-current flow of the gas–liquid. Energy consumption is relatively high because of pumping costs.

Ejector venturis may be used alone or as the first stage of a more complex system. The principal collection mechanism in this type of scrubber is inertial impaction, which is effected by liquid drops.

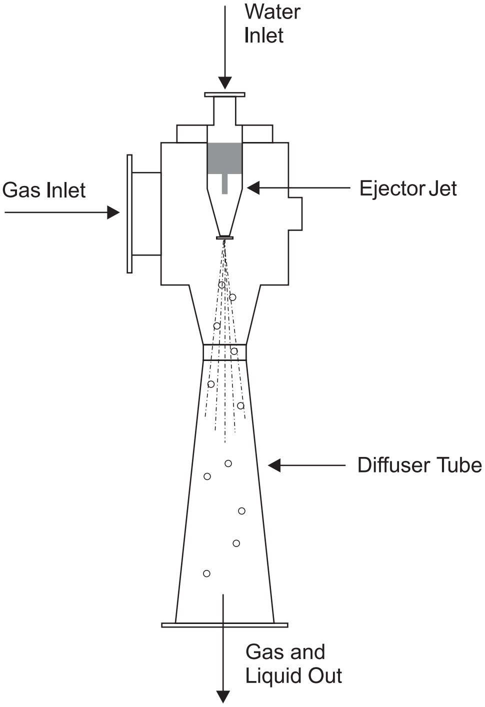

FIGURE 28.12 Water creates the energy for this ejector venturi scrubber.

Particle adherence upon striking droplets is dependent upon wettability of the particles. Because scrubbing liquid is usually recirculated, nozzles must be capable of handling a high solids concentration.

Wet Electrostatic Precipitators

Water can also be used with electrostatic precipitation to improve removal of particulates. In this type of system, water is continually recirculated over the plates, and discharged to an ash sluice pond or thickener to be clarified for reuse.

Waterside Problems

Operating conditions in the scrubber may produce severely corrosive or scaling water, depending on the gas stream being scrubbed and the nature of chemicals added to the water. Many systems use lime or limestone slurries to react with sulfur dioxide (SO_2), forming insoluble compounds removed in a thickener. Problems encountered in wet scrubber operations parallel those found in an open recirculating cooling water system, but scrubber water is often more saline.

Chemical treatment programs for wet scrubber systems are designed to:

- Maintain clean nozzles and collection surfaces, preventing deposit or scale buildup, thus helping to maintain unit efficiency
- Improve particulate capture or, for gas removal, mass transfer
- Control corrosion in the scrubber and recirculating water systems

Water problems in scrubbers range from scale and deposits to corrosion and waste disposal. Depending on the moisture level or dew point of the gas stream, gas cooling can result in evaporation or condensation, leading to concentration or dilution of scrubber water.

If the gas stream is above the dew point, recycling water for wet scrubbing results in evaporation and concentration of scrubber water, adding to corrosion and scale problems inherent with gases or particulates removed from the gas stream. However, in some systems, the gas contains substantial water vapor, and condensation with resultant dilution of recycle water may occur. This tends to lessen the potential for scale, deposits, and corrosion. Dilution is less common than concentration.

Each scrubbing system must be considered individually because of the wide variety of construction materials available, including mild and stainless steels, copper and nickel alloys, fiberglass, polyvinylchloride (PVC), ceramics, lead, and refractory, to name a few. Many manufacturers construct scrubbers of alloyed metals and nonmetallic materials to avoid corrosion problems but still encounter problems of scale and deposition. The same techniques and principles used for corrosion and deposit control in cooling water systems apply to scrubbers.

Scrubber systems that operate under low pH conditions, usually have deposits that are primarily particulates removed from the gas. Those systems that operate at a pH greater than 7.0 normally yield scale deposits produced from water reactions or scale and suspended solids combined.

However, even high-pH systems sometimes yield deposits that are primarily particulates removed from the gas. It is difficult to generalize regarding composition of deposits, because of the wide variability of scrubber designs, process gases, and water characteristics. The most commonly encountered deposits are calcium carbonate, calcium sulfate, lime [$Ca(OH)_2$], iron oxide, carbon black (soot), oils and greases, aluminosilicates (clays), and metal sulfides. Deposits, like corrosion, can plague virtually every section of the scrubber system from inlet gas ports to induced draft fan and stack. Deposits usually form at the venturi throat, trays, and packing in gas absorbers, liquid recycle lines and pumps, mist eliminators, induced draft fans, and clarifier supply lines.

Chemical treatment for scale and deposit control is effective in controlling the majority of deposits, but it must be individualized for each scrubbing system owing to variation in deposition problems.

Waste Treatment

Since the basic function of the wet scrubber is to remove contaminants from process and combustion gases, once scrubber liquid has done its job, disposal of contaminants transferred to the water must be considered. For the small plant, this may entail merely discharging a bleed-off of recycle water to the sanitary sewer. The larger plant may be required to install an in-plant clarification system.

There are two basic types of clarifier systems. The first is the full-flow, in-line clarifier that clarifies all scrubber water after it has made one pass through the scrubber. Water is recycled from the clarifier to the scrubber for further reuse. Problems are usually less severe with this type of unit, because suspended solids are usually maintained at a low level. This type of system is in many respects comparable to a once-through system.

The second type of clarifier is that used for clarification of a blowdown sidestream from the recycle system before discharge. Problems are normally more severe with this type of system.

Scrubbing liquid that contains high biochemical oxygen demand (BOD), heavy metals, or toxic matter may require additional treatment such as biological oxidation before discharge.

Auxiliary Equipment

Although the wet scrubber is the heart of the gas cleaning system, auxiliary equipment is required to help the scrubber work efficiently. Auxiliary equipment may be categorized as follows:

- Dust catchers remove gross solids to prevent overloading the scrubber.
- Gas quenchers cool high-temperature [over 1000°F (538°C)] gas and reduce evaporation in the scrubber.
- Entrainment separators (demisters) reduce water droplets in exit gas.
- Gas cooling towers reduce plume discharge.
- Cooling towers, cooling ponds, and spray ponds facilitate optimum water recycle and minimize makeup.
- Induced draft fans move gas from the scrubber to the discharge vent or stack.

- Forced draft fans move gas to the scrubber and through to the vent or stack.
- Gas reheat systems reduce plume discharge by raising the gas dew point.
- Clarifiers, thickeners, and settling ponds facilitate recycle and recover solids for disposal or reuse.
- Sludge dewatering devices consolidate recovered solids.

Selected Gas Scrubbing Systems

This section presents examples of gas scrubbing systems used in the electric utility, steel, and paper industries, including the basic types of scrubbers and auxiliary systems used in these applications and the nature of waterside problems.

SO_x Removal from Flue Gas

Flue gas desulfurization (FGD) is widely practiced to remove sulfur oxides (SO_x) from boiler stack gas, particularly in the electric utility industry. Wet limestone scrubbing is a popular FGD method.

Chemistry of Flue Gas Desulfurization

The FGD process uses alkali (limestone) to react with and neutralize acidic sulfur gases. For this discussion, sulfur dioxide (SO_2) is used.

The first step in the neutralization process is to absorb SO_2 into the spray water as shown in Eq. (28.1):

$$SO_2 + H_2O \rightarrow H_2SO_3 \tag{28.1}$$

Sulfurous acid (H_2SO_3) can undergo dissociation as shown in Eq. (28.2):

$$H_2SO_3 \rightleftharpoons H^+ + HSO_3^- \rightleftharpoons 2H^+ + SO_3^{-2} \tag{28.2}$$

Addition of limestone ($CaCO_3$) slurry neutralizes the acidity of SO_2, producing calcium sulfite ($CaSO_3$):

$$H_2SO_3 + CaCO_3 \rightarrow CaSO_3 + CO_2 + H_2O \tag{28.3}$$

Under conditions maintained in the scrubber, $CaSO_3$ precipitates as the hemihydrate:

$$Ca^{+2} + SO_3^{-2} + 1/2\,H_2O \rightarrow CaSO_3 \cdot 1/2\,H_2O \tag{28.4}$$

Proper pH control in the scrubber is critical for performance. Many FGD scrubbers operate at pH 5.6 to 5.8. If scrubber water pH is too low, SO_2 removal decreases. If scrubber water pH is above 6.0, limestone feed is too high, which affects operational costs.

Generally, flue gas contains excess oxygen to assure complete combustion of fuel. Excess oxygen reacts with bisulfite (HSO_3^-) and sulfite (SO_3^{-2}) to form sulfates:

$$SO_3^{-2} + 1/2\ O_2 \rightarrow SO_4^{-2} \tag{28.5}$$

Experience indicates that the first 15 mole percent of sulfate ions co-precipitate with sulfite to form calcium sulfite–sulfate hemihydrate ($0.85CaSO_3 \cdot 0.15CaSO_4 \cdot ½H_2O$). Sulfate above 15 mole percent precipitates as gypsum:

$$Ca^{+2} + SO_4^{-2} + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O \tag{28.6}$$

Chemistry control of scrubber water markedly affects potential scale formation in the spray tower. Experience indicates that scale can be minimized or even prevented when scrubber water is operated in a completely oxidized state (no calcium sulfite–sulfate hemihydrate formation) or in a completely nonoxidized state (no gypsum formation). Therefore, most FGD installations operate in one of these two modes to avoid scale formation and the associated costs of reduced throughput and downtime for cleaning.

The completely oxidized state is more popular because the product (gypsum) is easier to handle and can be sold. Calcium sulfite–sulfate hemihydrate is a soft solid that is difficult to dewater and does not have good market value. Gypsum, on the other hand, can be vacuum filtered to produce a relatively dry cake. Wallboard manufacturers find this gypsum source attractive due to its purity and uniform particle size. Therefore, gypsum production from FGD systems has good market value. Gypsum production can be maximized by installing forced air oxidation systems to convert all sulfite ions to sulfate ions.

Flue Gas Desulfurization Scrubber Design

Design of FGD scrubbers has undergone many changes during evolution of this technology. Originally, FGD scrubbers contained packing, and many installations still do. However, packing is prone to scaling during chemistry upsets. Newer designs reduce the amount of packing or even eliminate packing entirely, by using spray nozzles to create intimate contact between flue gas and scrubber water. Figure 28.13 shows an FGD open spray tower design.

Even with forced air oxidation to generate only gypsum, a number of operating issues still present challenges:

- Scale formation during chemistry upsets
- Spray nozzle efficiency and plugging

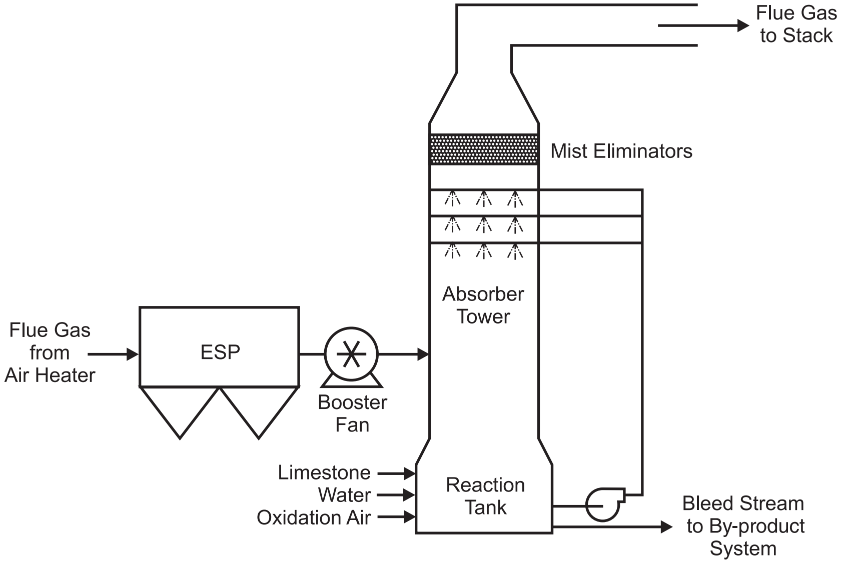

Figure 28.13 Utility stack gas scrubbing system.

- Mist eliminator performance and maintenance
- Limestone quality, particle size, reactivity, and additives for improved performance
- By-product disposal or sale, including both cake and liquid

Limestone represents a significant operating cost in FGD systems, and optimization of limestone use is a key operating concern. Poor limestone reaction leads to increased limestone feed, which increases operating costs. Some factors that affect limestone reactivity and use include: quality, particle size, residence time, and solids–liquids separation in the scrubber water.

FGD designs continue to evolve. New systems, such as the Chiyoda process, provide new methods to contact flue gas with limestone slurry and attempt to address operating issues of existing FGD systems.

SECTION 4

Energy in Water Systems

CHAPTER 29
Energy Use in Effluent Systems

CHAPTER 30
Energy in Cooling Systems

CHAPTER 31
Energy in Steam Systems

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CHAPTER 29

Energy Use in Effluent Systems

The U.S. Environmental Protection Agency (EPA) estimates that 0.1 to 0.3% of the nation's total energy usage is consumed in municipal and industrial effluent treatment. Energy costs can account for 30% of the operations and maintenance budget of a typical municipal effluent treatment facility, second only to staffing costs. By comparison, chemicals represent about 4% of the same budget category. Electrical energy accounts for over 90% of the total energy consumed in effluent treatment. Fuels such as oil and natural gas are sometimes used for onsite generation of electricity, but in most instances, electricity is supplied by independent remote generators. Interestingly, effluent treatment can be a producer of energy. Anaerobic digestion, which generates combustible biogas (a combination of methane and carbon dioxide), and even flowing water, typically at the outfall, can be utilized as energy sources. That said, other than a handful of demonstration facilities, no effluent treatment plant is completely self-sustaining with regard to energy, and most are net users of energy and in particular electrical energy.

The focus of this chapter is on primary, secondary, and tertiary effluent treatment with a particular emphasis on aeration within the activated sludge process. Solids processing, including thickening, stabilization and dewatering, although significant in terms of energy, is not covered. In addition, management of utility rate structures, although a critical part of any discussion on energy use and optimization, is not discussed. One typical example of managing the utility rate structure involves shifting some processes to off-peak hours to take advantage of lower energy rates. In reality, this often requires ability to store effluent or biosolids, and in many instances, that is not an option.

Finally, study of energy in effluent treatment is multifaceted and covers an incredible amount of equipment, plant configurations, operating strategies, and regulatory issues. This diversity is equaled only by the amount of information and support now available. The EPA and U.S. Department of Energy (DOE) are useful resources to launch a more focused investigation into the subject.

Energy Utilization in Effluent Treatment

Electrical energy is used to power many different types of processes and equipment at a typical effluent treatment facility. Major energy consumers include pumps, blowers, mechanical aerators, and solids handling systems. In most cases, blowers and pumps claim the most electrical energy. Pumps are used to move effluent and often sludge from one point to another, when gravity flow is not feasible or possible. Blowers are used to move air and provide one of the ways effluent is aerated. Air can also be used in various physical separation processes like dissolved air flotation (DAF); however, its predominate use is in aeration. Figure 29.1 shows approximate breakouts of electrical energy costs at a typical municipal activated sludge effluent treatment plant.

Realize that activated sludge processes treat roughly 90% of municipal effluent in the United States and represent the predominant treatment approach in many industrial applications including hydrocarbon, chemical, paper, and food processing. The predominance of activated sludge systems is due to an optimum balance between throughput, effluent quality, sludge generation, and overall cost of treatment. Other common treatment platforms include fixed-film systems like trickling filters, rotating biological contactors (RBC), and ponds. Each of these configurations has its own unique energy signature.

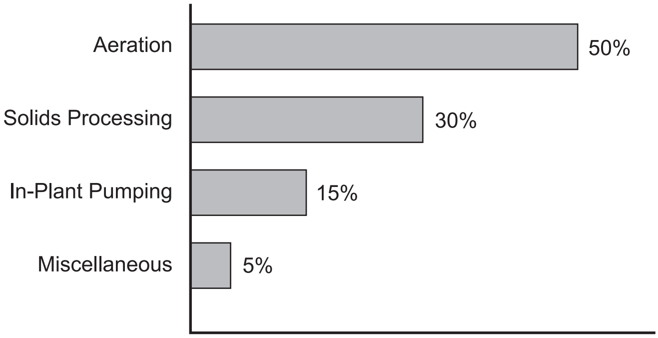

FIGURE 29.1 Electric energy breakout at municipal activated sludge facility.

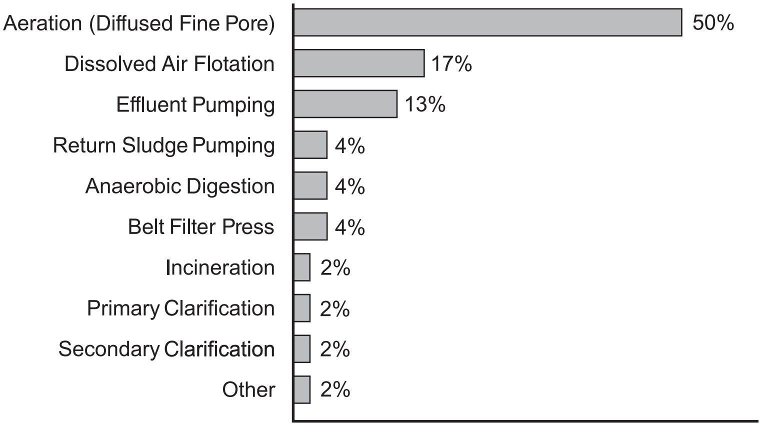

FIGURE 29.2 Electrical energy usage distribution in 10 mgd (26 m^3/min) municipal activated sludge facility with 437 kW power requirement.

Figures 29.2 to 29.4 show the indexed percentage of electrical energy consumed by various processes and operations at typical 10, 20, and 100 mgd (26, 53, and 263 m^3/min, respectively) municipal activated sludge facilities. The disproportionate percentage attributed to aeration, diffused aeration in this case, underscores the importance and reliance on aerobic treatment in effluent. Figures 29.5 to 29.7 show the indexed percentage of electrical energy consumed in similarly sized plants featuring a trickling filter process, which is a common treatment approach in municipal effluent treatment. Note that in this configuration, pumps consume the largest percentage of energy, as effluent must be continually circulated over static media.

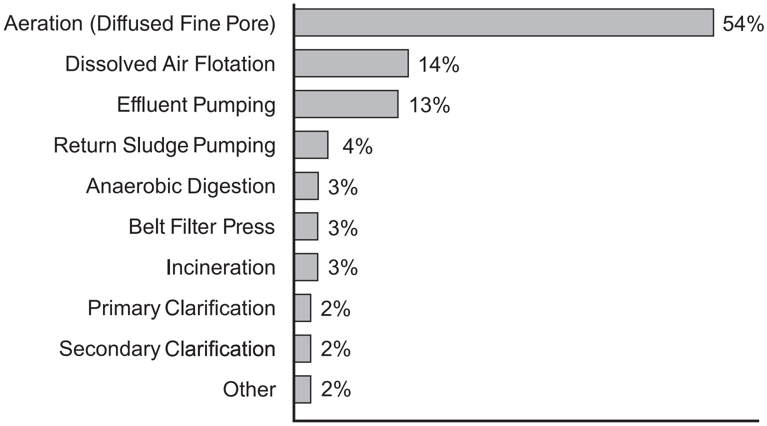

FIGURE 29.3 Electrical energy usage distribution in 20 mgd (53 m^3/min) municipal activated sludge facility with 811 kW power requirement.

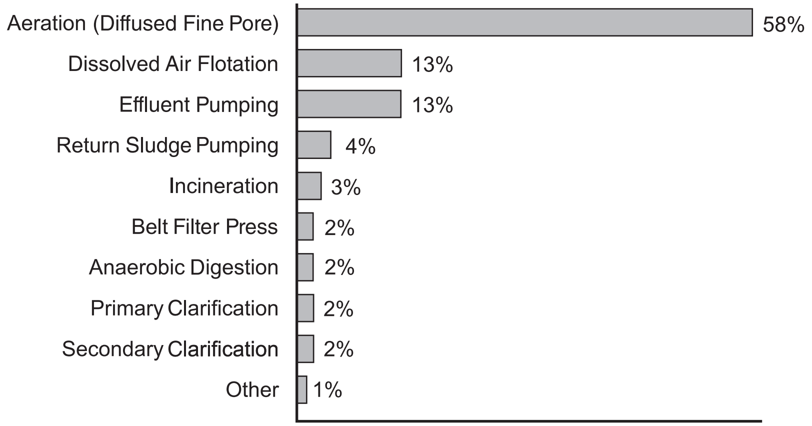

Figure 29.4 Electrical energy usage distribution in 100 mgd (263 m^3/min) municipal activated sludge facility with 3.8 MW power requirement.

Energy savings opportunities exist to some degree, at most effluent treatment facilities. There is increasing focus from many diverse constituencies concerning energy conservation in effluent treatment. Familiar programs like EPA Energy Star have identified effluent treatment as a focus sector among other significant users of electrical energy. A key element of the program is an online tool that allows operators (currently limited to municipal facilities) to enter equipment and operating dimensions relative to their particular plant, and get a ranking of energy usage based on a comparison to similar plants. However, variables like strength of effluent, treatment process,

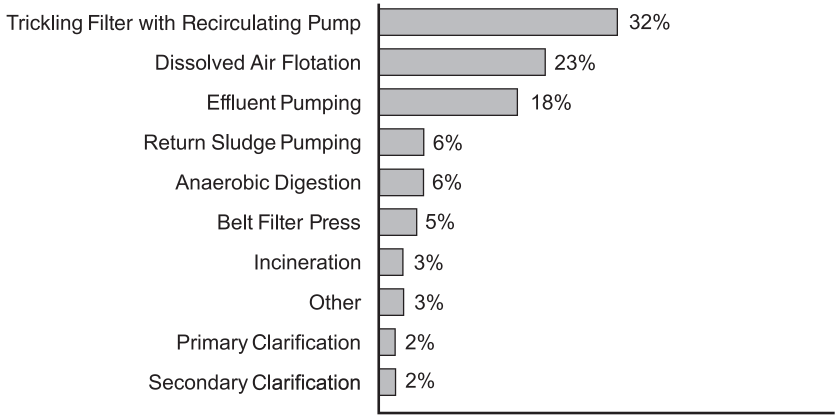

Figure 29.5 Electrical energy usage distribution in 10 mgd (26 m^3/min) municipal trickling filter facility with 321 kW power requirement.

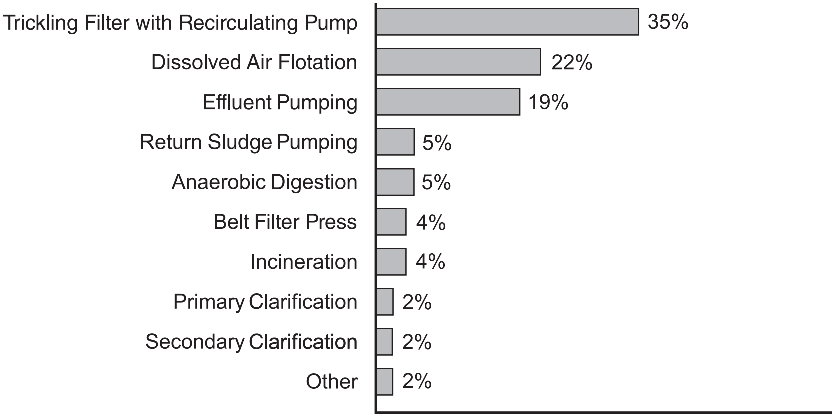

FIGURE 29.6 Electrical energy usage distribution in 20 mgd (53 m^3/min) municipal trickling filter facility with 563 kW power requirement.

level of treatment, operational and maintenance choices, regulations, and current state of energy conservation initiatives make broad generalizations about energy use in effluent treatment challenging. This fact is even more pronounced in industrial effluents, including those found in food processing, paper, and refining, where all of these variables are more diverse.

An energy audit is certainly a good first step in understanding energy usage, and can be valuable even when done at a modest level. For example, questions like those below could be used to begin an evaluation of key pieces of equipment and processes. The answers to these questions help determine what processes can be modified

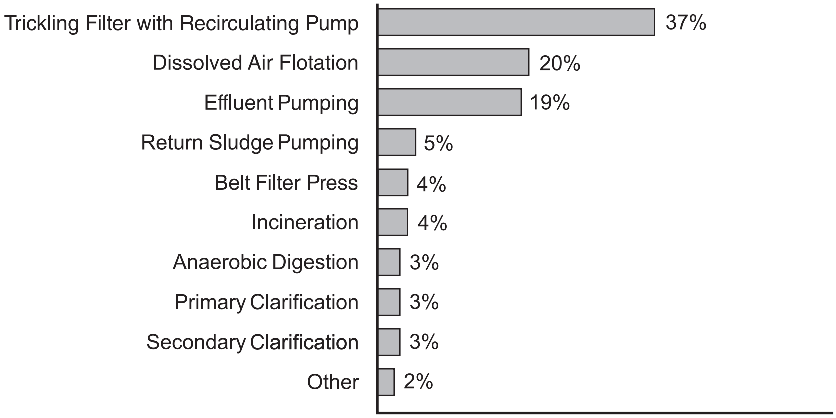

FIGURE 29.7 Electrical energy usage distribution in 100 mgd (263 m^3/min) municipal trickling filter facility with 2.5 MW power requirement.

or what equipment can be operated more efficiently, or replaced to save energy.

- Does the process or equipment need to run at all?
- Is it possible to run the process or equipment for fewer hours?
- Is it possible to shift this activity to off-peak hours (for some auxiliary functions)?
- Are energy efficiency process modifications or equipment upgrades practical and possible while maintaining equipment efficiency?
- What equipment is most energy efficient for this process?

Is it possible to run more efficient pumps for normal base loads, or to use lower efficiency larger units for only peak flows?

Motors

Motors provide the means to rotate impellers found in pumps and blowers. Recall that pumps move liquids and sludge in effluent treatment, while blowers move air. Taken together, pumps and blowers can account for more than 80% of the total electrical energy consumed in an effluent treatment plant. Because of their high efficiency and low maintenance requirements, three-phase squirrel cage induction motors are most prevalent.

Motors are rated in units of power (horsepower or watts) based on the maximum amount of work they are capable of performing. Actual power consumed at any given time by an operating motor is in direct proportion to the work being performed. The primary goal in choosing a motor is to be sure the motor selected has adequate power to drive the intended load throughout the entire anticipated load range. In general, motors are usually specified 10 to 20% larger than actually required. A secondary goal is that the motor be energy efficient and economical.

The Energy Policy Act of 1992 set out to establish standards for energy efficient motors. Energy efficient motors consume less energy and can lead to a significant decrease in operational costs as compared to standard motors. This is possible because of design improvements and more accurate manufacturing tolerances. They are more durable, have an overall longer lifetime, lower heat output, less noise and vibration, and improved tolerance to over-voltage. Energy efficient motors typically cost 10 to 30% more than standard motors, but can be up to 8% more efficient.

In 2001, the National Association of Electric Manufacturers (NEMA) implemented a new NEMA Premium® Efficiency Motor Standard. Under this voluntary program, a motor may be marketed as a NEMA Premium motor if it meets or exceeds a set of NEMA minimum full-load efficiency levels. Note that these levels are higher than the minimum full-load efficiency standards for energy efficient motors under the Energy Policy Act of 1992.

Energy efficient motors should be considered for all new purchases and replacements; however, selecting the proper motor size can be complicated and compounded by factors that are not immediately obvious and beyond the scope of this book.

Variable Control Devices

Variable control devices are typically located between the driver or motor and driven element, like an impeller, and are often referred to simply as drives. Categories of drives include mechanical, electromechanical, and electronic devices. Direct current (DC) motors can be controlled with variable resistance drives like rheostats, which decrease current to the motor resulting in decreased power to the motor. Alternating current (AC) motors can be equipped with drives that provide variable voltages or variable frequencies. Current industry preference is for variable frequency drives (VFD) because of their high efficiency, good reliability, and reasonable economics.

The key benefit of a VFD is that it allows motor speed to be matched to demands of the work being performed, which can often result in energy savings. For example, a VFD allows more precise control of processes such as aeration and sludge pumping. Relative to single speed motors, a VFD permits gradual ramp up to operating speed. This lessens mechanical and electrical stresses on the motor system, and can reduce maintenance and repair cost, extending motor life. A VFD can reduce energy use of a pump by as much as 50%, but this benefit is highly dependent on system variables like pump size, static head, friction, and flow variability. Consequently, it is important to examine each application before specifying a VFD. For example, a large effluent treatment plant may be better served by having constant speed pumps for the base load, and perhaps one pump with variable control to respond to changing flow conditions.

Aeration

Overall, aeration and related operations are the single most significant consumer of electrical energy in most secondary and advanced effluent treatment facilities. Estimates put the cost for electrical energy for aeration in the 40 to 60% range or greater, of the total electrical energy consumed. Aeration is necessary to support aerobic respiration, and to keep contents of the aeration basin sufficiently mixed. In most instances, meeting the aeration requirement satisfies the mixing requirement. Note that aeration is used in aerobic sludge digestion, and in some physical separation processes like DAF that are unrelated to aerobic respiration. In general, these uses are small by comparison.

The amount of oxygen required is factored from carbonaceous demand, endogenous demand, nitrogenous demand, initial dissolved oxygen (DO) deficit, and degree of stabilization required. Determining initial oxygen requirements for a new activated sludge system is usually based on conservative analysis, featuring a large safety factor to ensure adequate oxygen supply is always available for peak load conditions.

Aeration power requirements can be calculated once loading, flow rates, and equipment oxygen transfer performance are known. To illustrate this concept, consider that the aeration power requirement is expressed by Eq. (29.1).

$$E = QdL/q \tag{29.1}$$

where E = aeration power requirement, hp (kW)
Q = flow, mgd (m^3/h)
d = density of liquid, lb/gal (kg/L)
L = loading, mg/L
q = standard aeration efficiency (SAE), lb O_2/[hp·h] (kg O_2/kWh)

For example, oxidation of 300 mg/L biochemical oxygen demand (BOD) in a 10 mgd (1577 m^3/h) municipal effluent treatment plant using aeration equipment with SAE of 2.5 lb O_2/[hp·h] (1.52 kg O_2/kWh) would suggest the following power requirement.

U.S. Units

$$\begin{aligned} E = {} & (10 \text{ mgd})(8.33 \text{ lb/gal})(300 \text{ mg/L})/ \\ & (2.5 \text{ lb } O_2/[\text{hp}\cdot\text{h}])(24 \text{ h/d}) = 417 \text{ hp} \end{aligned}$$

Metric Units

$$\begin{aligned} E = {} & (1577 \text{ m}^3/\text{h})(1 \text{ kg/L})(300 \text{ mg/L})(1000 \text{ L/m}^3)/ \\ & (1.52 \text{ kg/kWh})(10^6 \text{ mg/kg}) = 311 \text{ kW} \end{aligned}$$

Note that design safety factors increase the calculated power requirement further.

Operators typically use mixed liquor dissolved oxygen (MLDO), commonly referred to as just DO, in managing the aerobic process. Conveniently, there is rarely a need to operate an activated sludge process at a DO concentration above 2 mg/L. It is possible to operate successfully at DO concentrations closer to 1 mg/L with 1 to 1.5 mg/L being a good operational range to target. Caution should be exercised when the DO level approaches 0.5 mg/L, and as a rule, DO should never be allowed to drift below 0.5 mg/L. At the other extreme, excess aeration, aside from being costly, can interfere with flocculation, causing poor settling in the secondary clarifier. Although establishment of a DO target is a reasonable approach, various factors can affect efficiency of oxygen transfer and use and more importantly, efficiency of energy use. For example, the number of aeration tanks in service, air rate per diffuser, presence of nitrification when not required, food-to-microorganism ratio (F:M), aerator submergence, and air cleanliness can all affect overall efficiency.

Finally, there are special situations, often found in processes downstream of secondary treatment that endeavors to establish different respiratory pathways. For example, in biological denitrification, an anoxic environment is created to establish nitrate (NO_3^-) as opposed to molecular oxygen (O_2) as the ultimate electron acceptor.

Aeration Equipment

Transfer of oxygen from air to waste or effluent is relatively inefficient and energy intensive. The fraction of oxygen in air bubbles supplied by aeration equipment that dissolves in clean water is called the standard oxygen transfer efficiency (SOTE). SOTE divided by energy used per unit weight of oxygen delivered is the SAE. SAE expresses the weight of oxygen dissolved per unit of energy used by aeration equipment. Actual or field oxygen transfer efficiency (FOTE) differs from SOTE because real conditions differ from test conditions. The ratio of normalized FOTE to SOTE, literally the ratio of the oxygen transfer rate in effluent to that in clean water, is referred to as the alpha factor. The alpha factor can be influenced by many variables. For example, surfactants typically depress FOTE and reduce alpha to below one. Strict rules for performance testing of aeration equipment have been established by independent groups such as the American Society of Civil Engineers (ASCE). Most equipment manufacturers follow these rules when evaluating and representing their products.

Diffused Aeration

Diffused aeration delivers compressed air through submerged porous or perforated diffusers that create bubbles, ultimately transferring oxygen as they rise. Deeper tanks enhance oxygen transfer efficiency (OTE) by lengthening bubble rise and increasing hydrostatic pressure on the bubbles, both of which hasten oxygen transfer. However, increasing hydrostatic pressure requires more blower capacity and energy along with greater capital expenditure.

There are two general categories of diffusers: course bubble and fine bubble. The number of bubbles produced per unit volume of air and bubble diameter differentiates the two systems. EPA defines fine bubble diffuser equipment as its ability to produce bubbles with an average diameter of 2 mm. Course bubble diffusers (Fig. 29.8) generally represent older technology, and they are typically less costly to construct and maintain. SAE for course bubble diffusers is about 2 to 3 lb O_2/[hp·h] (1.2–1.8 kg O_2/kWh).

Figure 29.8 Typical coarse bubble diffuser.

Fine bubble diffusers (Fig. 29.9) have grown in popularity because of rising energy costs. Smaller diameter bubbles produced by fine pore diffusers provide more surface area per volume, thereby facilitating higher OTE values. Furthermore, small bubbles tend to rise more slowly, and additional contact time increases OTE. However, fine bubble diffusers cost more initially, require cleaner air, and usually require more maintenance than course bubble diffusers. They are typically constructed in the shape of plates, discs, domes, or tubes made of plastic or ceramic. In some installations, flexible sheath tubes are used. Fine pore diffusers have SAE of 4 to 7 lb $O_2/[\text{hp}\cdot\text{h}]$ (2.4–4.3 kg O_2/kWh), with some advanced membrane systems reaching even higher efficiencies. Fine pore systems, when operating at peak efficiency, can use as a minimum 25% less energy than course bubble or mechanical counterparts. Simple payback economics of fine bubble retrofits are quite favorable in the 2 to 5-year range. As expected, payback is shortest in situations where electrical energy costs are highest. The biggest potential negative factor in considering a fine bubble system involves increased maintenance costs due to fouling.

All diffusers are subject to fouling from the waterside, airside, or both. Significant fouling wastes energy and reduces ability of the system to deliver sufficient oxygen to the basin. Course bubble diffusers have relatively large orifices and consequently are less prone to fouling with air or waterside impurities. Natural fouling that tends

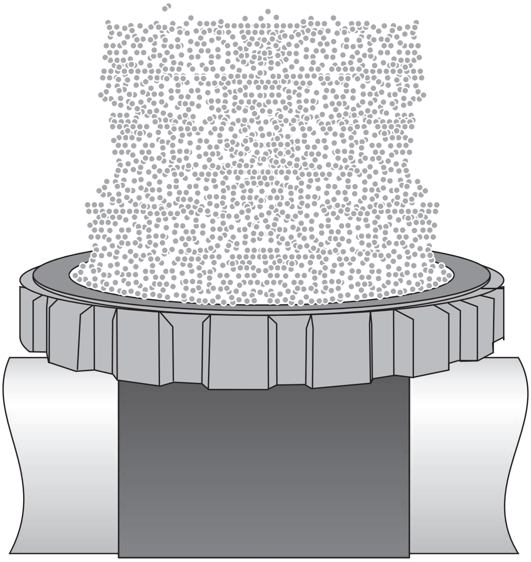

FIGURE 29.9 Typical fine bubble diffuser.

to occur in course bubble diffusers can be reversed to a large degree by periodically blowing out diffusers with excess air. Fine bubble diffusers are more problematic because their smaller diameter pores are more easily fouled. Air-side fouling is often the result of poor air filtration and other material originating after filtration. Foulants can include dust, dirt, rust, and scale from air pipe corrosion, construction debris due to poor cleanup, and mixed liquor solids entering through leaks and breaks. Water-side fouling can occur from precipitated solids, biological growth, organic and inorganic material entering the media at low or zero pressure, oils and grease, etc.

Detection and rate of diffuser fouling is of obvious importance. Historically, a rise in backpressure signaled fouling. While overall system pressure monitoring serves as an indicator of extreme fouling, it lacks sensitivity, particularly relative to increased diffuser head loss. Buildup of head loss and flux rate, defined as airflow rate per diffuser(s) divided by the effective diffuser area, may have a significant effect on aeration system capacity or OTE. Further, fouling of only a portion of the diffuser area may lead to substantial redistribution in airflow, but little increase in overall system pressure. Today, better methods exist to measure performance of operating aeration systems, allowing for more effective preventive and maintenance programs. For example, dynamic wet pressure (DWP) can allow measurement of head loss across the air distribution control orifice and across the diffuser. Head loss across the orifice is used to determine the rate of flow through the diffuser, while head loss across the diffuser media indicates the degree to which the diffuser has been fouled. Note that heavily fouled fine bubble diffusers have OTE comparable to course bubble diffusers.

Methods of cleaning fine pore diffusers can be in situ or ex situ. In situ means diffusers are cleaned in the basin, either drained or full, while ex situ means diffusers are removed from the basin. Ex situ methods include refiring of ceramic diffusers, high-pressure water jetting, and washing with silicate–phosphorous, alkali, acid, or detergent. Ex situ methods are expensive and reserved for situations that do not respond to less invasive approaches. In situ methods include physical, chemical, and biological procedures. Diffusers may be physically washed with water, air, or steam. Chemical options include treatment with gaseous compounds like hydrogen chloride, chlorine, or gaseous biocides applied to the air side and liquid acid or detergent for cleaning of diffuser surfaces. Choice of cleaning method is often by trial and error.

Where fine bubble systems have replaced mechanical aerators, aeration basin geometry and the need to install blowers and air piping are important considerations. Where fine bubble systems have replaced course bubble diffusers, air systems are usually more than adequate, since fine bubble diffusers provide a higher OTE. Sometimes, an activated sludge plant capacity can be increased by a fine bubble retrofit, particularly if the plant is aeration limited.

Mechanical Aeration

Mechanical aerators are commonly divided into various categories, but essentially, they all use motors to rotate propellers, blades, or brushes that reside close to the surface of the effluent, or slightly submerged, to vigorously move the water, thereby increasing diffusion of oxygen into water (Figs. 29.10 and 29.11). These devices are typically driven by an electric motor either directly or through some type of transmission or gearbox that can be horizontal or vertical relative to the rotating element. Mechanical aerators can be expected to have SAE of 2 to 4 lb $O_2/[\mathrm{hp \cdot h}]$ (1.2–2.4 kg O_2/kWh), which is similar to course bubble diffusers; however, mechanical systems are observed to have slightly higher efficiencies. Options for adjusting air delivery to oxygen demand include submergence adjustment, speed adjustment, and powering up and down.

Aeration Control and Monitoring

The most common cause of aeration system inefficiency is excessive DO in mixed liquor. Due to oversized equipment, inefficient operation, or lack of controls, the amount of air delivered to the aeration basin is often much more than required for supporting aerobic respiration or mixing. Excess air represents wasted energy, and highly aerated effluent can lead to settling problems and solids carryover.

Figure 29.10 Details of construction of a fixed-position surface aerator, shaped to produce high-volume pumping and air entrainment. (*Courtesy of Infilco Degremont Inc*.)

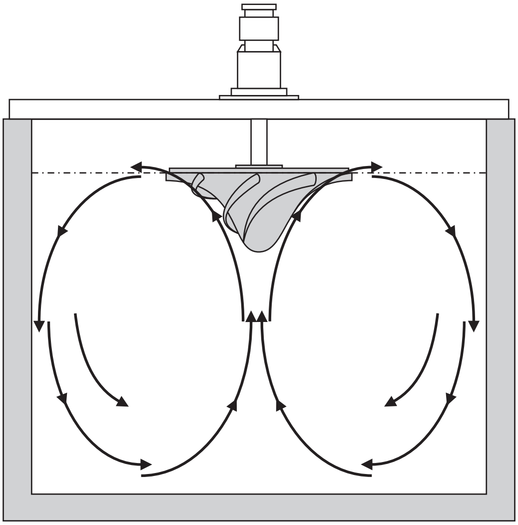

Figure 29.11 Typical flow pattern of a surface aerator. Sufficient mixing in the basin is very important for good aeration.

Use of DO probes in aeration tanks with blower feedback control systems and variable speed drives can result in substantial energy cost savings with relatively modest payback periods. Ideally, air delivery is controlled to match instantaneous oxygen demand relative to a set point. Automated controls can match air delivery to oxygen demand, more accurately and efficiently than manual controls. It is not uncommon to achieve a 20% energy savings after retrofit with monitoring and automatic controls. Payback can be expected to fall in the 1 to 4-year timeframe, with larger facilities achieving payback sooner. However, DO probes require careful selection, placement within the basin, calibration, process monitoring, and maintenance, and as a result, some operators have resisted their deployment and use.

Aeration system controls can be applied to either mechanical or diffused aerators, but are more likely to be installed on diffusers. Capital cost of a control system for course bubble aerators is higher than that for fine bubble systems, because the former likely has larger motors and variable speed drives.

Preliminary and Primary Effluent Treatment

Primary effluent treatment including treatment ahead of the primary treatment process, sometimes called preliminary treatment, is mainly responsible for removing settable solids and floating material from effluent. Primary treatment typically removes 50 to 60% of total suspended solids (TSS) and 30 to 40% of BOD in the influent.

The typical primary settling tank, often referred to as primary clarifier, employs relatively small motors for various mechanisms and pumps. This equipment may include primary sludge pumps, collectors, skimmers, and sprays. Because primary treatment relies on gravity separation, energy requirements are usually relatively small.

Primary sludge pumping is typically the largest energy consuming operation in primary treatment. One energy conserving measure (ECM) available in primary treatment is to ensure that primary sludge pumping rates are adjusted to match primary sludge accumulation, generally a function of flow in the primary clarifier.

One of the most ignored but potentially beneficial ECM’s available to effluent treatment facilities is to address poor removal, including both BOD and TSS, in primary treatment. Poor removal can lead to greater use of energy in secondary treatment and other downstream processes. For example, dye tests conducted at one facility revealed that improving the flow split to multiple clarifiers, and installing baffles to reduce clarifier short-circuiting improved BOD removal significantly. This, in turn, reduced BOD loading and corresponding oxygen demand in secondary treatment, leading to more cost-effective operation.

One notable exception with regard to modest energy use in primary treatment can be found in instances where air is used to assist in the separation process. Examples include aerated grit chambers found in municipal effluent treatment, and DAF units found in effluents typical of the hydrocarbon and food processing industries. These operations can use considerable amounts of energy, and reducing blower output could result in reduced in energy use. However, matching blower output with the optimum air requirement is largely a trial and error process.

Recycle flows should be inventoried, as they can undermine the relatively energy efficient primary treatment process. For example, anaerobic digester decant is often sent to primary treatment, where it can initiate biological activity, and undermine performance of the primary treatment process. Other potential flows include sludge dewatering supernatant, and sludge drying bed drainage. Off peak treatment of these flows, if possible should be evaluated. Finally, intermittent use of air and water sprays for foam and scum control should be considered as opposed to their continual use.

Chemicals can be used to enhance primary treatment, and should be selected on a cost performance basis. In general, primary treatment offers a more energy efficient way to remove contaminants, and operators should seek to maximize removal potential of primary treatment. That said complete accounting of energy necessary to process primary treatment solids should be included.

Secondary Effluent Treatment

Following preliminary and primary treatment, effluent contaminants consist primarily of colloidal matter that is highly organic, along with small amounts of dissolved organic matter, nutrients, and dissolved inorganic solids. As defined by the Clean Water Act (CWA), secondary treatment should produce effluent with not more than 30 mg/L BOD and 30 mg/L TSS.

The primary operational objective of secondary effluent treatment is to create and maintain an aerobic environment. Secondary treatment processes can remove up to 90% of BOD in effluent by utilizing biological processes. Since the two have significantly different oxygen requirements and therefore energy requirements, BOD can be further divided into carbonaceous BOD, and nitrogenous BOD. Historically, BOD is determined experimentally by measuring oxygen uptake over a 5-day period and noted as BOD_5. During this time, biodegradable organic carbon is biologically oxidized, while oxygen is reduced proportionally. Note that for practical purposes, this test, in terms of time, is often shortened and results extrapolated.

Chemical oxygen demand (COD) is another measure for evaluating effluent. Unlike BOD, COD represents all oxidizable material in water. COD is always greater than BOD, and more importantly, some percentage of COD cannot be removed biologically.

High electronegativity (measure of the attraction for electrons) of oxygen creates a large potential energy drop for cellular respiration, allowing organisms using aerobic respiration to produce much more adenosine triphosphate (ATP) than anaerobic organisms, thereby making aerobic respiration more favored. Aerobic respiration makes possible stabilization of large quantities of contaminants found in effluent. These contaminants can be quickly and efficiently oxidized, or destroyed, with carbon dioxide, water, and new cell mass as the only tangible respiration by-products.

Bacteria in an effluent treatment plant comprises both heterotrophic and autotrophic microorganisms. Heterotrophic or carbonaceous bacteria are the predominant group of organisms. They are characterized by feeding mainly on organic carbon molecules rather than inorganic ones. By contrast, autotrophic microorganisms take in inorganic chemicals and use them in synthesis of organic compounds. Nitrifying bacteria, known by their ability to remove ammonia and ammonia compounds from effluent, are the most important of this group. There are fewer known species of autotrophic microorganisms, and since they have relatively slower growth rates, they tend to be out-competed by faster growing heterotrophic microorganisms. Often, effluent facilities use bioaugmentation, the purposed addition of bacterial cultures, when nitrification has been reduced or is not ongoing.

Without artificial introduction of air into effluent, by some method, the DO level would fall, and aerobic respiration would cease to be the predominant respiratory pathway. As discussed earlier, the process of dissolving oxygen in effluent is complex, relatively inefficient, energy intensive, and complicated by many factors including diffuser device type, basin geometry, diffuser depth, turbulence, ambient air pressure, temperature, spacing and placement of aeration devices, variations in flow, and loading.

Finally, most secondary treatment systems employ a secondary clarifier for capture and recirculation of solids generated in the aeration basin. Secondary clarifiers are not large consumers of energy and have energy requirements close to that of primary clarifiers. However, excess pumping of return activated sludge (RAS) is one area that should be investigated for potential energy savings.

There are numerous processes available for secondary effluent treatment, but most can be categorized as suspended growth or fixed film.

Suspended Growth Processes

Activated sludge, oxidation ditches, sequential batch reactors (SBR), and membrane bioreactors (MBR) are all examples of suspended growth systems. The most recognized and predominant suspended growth example can be found in the activated sludge configuration, although it is interesting to note that MBR are the fastest growing segment, albeit from a much smaller base. As mentioned previously, activated sludge systems treat roughly 90% of municipal effluent volume in the United States, and represent the predominant treatment approach in many industrial applications. In suspended growth processes, microbial growth is predominantly planktonic. Suspended growth processes sustain a viable population of target microorganisms by carefully controlling various parameters such as DO level, substrate concentration (food), mixed liquor volatile suspended solids (MLVSS), RAS pumping rate, waste activated sludge (WAS) pumping rate, temperature, toxicity, and nutrients.

One key variable strongly associated with energy usage in suspended growth processes like activated sludge is mean cell residence time (MCRT), or sludge age as it is also known. Simply put, MCRT is a measure of how long a microorganism has been in the secondary treatment process. To understand this concept, consider that viable microorganisms that comprise MLSS of an activated sludge process are in either the active stages of BOD removal and cell proliferation, or what is known as the endogenous phase of their life cycle. In both cases, oxygen is consumed, but only in the former is significant BOD removal underway. Shortening the MCRT has the effect of limiting microorganisms that are in the endogenous growth phase, thereby making the process with respect to BOD removal more aeration energy efficient. However, this concept has several drawbacks, including the fact that more solids are generated due to increased sludge wasting. Settling may be negatively affected, and there may be insufficient time for nitrification. For example, poor settling may require additional chemicals, while increased solids have a negative effect on solids handling operations, particularly where disposal costs are high. In essence, a trade-off is created between aeration and solids generation and treatment.

Fixed Film

Trickling filters and RBC are the primary forms of fixed-film systems. These systems use pumping energy in the case of trickling filters and mechanical energy in the case of RBC to introduce oxygen into effluent. In the case of a trickling filter, effluent is allowed to flow over static media like rocks or plastic. To be effective, effluent is often pretreated and pumped multiple times over the media, sometimes equaling three times the daily influent flow. In the case of RBC, media rotate with a portion exposed to effluent and the alternating portion exposed to air. Often, effluent is circulated by pump within the basin. Fixed-film processes use less energy than suspended growth processes, as seen previously in Figs. 29.2 through 29.7, but do not achieve as high a treatment level. As an example, a 100 mgd (263 m^3/min) tricking filter facility would likely have a total electrical energy cost in the neighborhood of 20% less than its activated sludge counterpart. However, fixed-film systems are prone to odors and often require additional equipment to address these odors. Once odor control systems are installed, the relative energy efficiencies, or at least overall operating costs, of fixed-film processes begin to approach those of suspended growth processes.

Tertiary Effluent Treatment Processes

There are various processes within effluent treatment that aim to achieve even higher effluent quality or address an aspect of treatment that may be difficult to achieve within the secondary effluent treatment process. Some ways in which these objectives can be satisfied include filtration, carbon adsorption, and chemical treatment. In general, these operations lead to a relatively insignificant contribution to total energy usage. That said, biological nutrient removal (BNR) could significantly add to the energy burden of an effluent treatment facility.

BNR can be managed as part of tertiary treatment and continues to be an area of focus and increasing regulation. Achieving targets for nutrient removal can put additional energy load on a facility, depending on the removal strategy. Both phosphorous and nitrogen can be removed biologically, although it is probably more practiced with nitrogen removal. Historically, phosphorous has been removed from effluent by chemical precipitation with metal salts. Biological processes can be used, whereby anaerobic selectors stress microorganisms before their return to the aeration basin. Stressed microbes then take up more phosphorous than they would under more normal conditions.

Nitrogen is often removed by biological nitrification and denitrification. Oxygen requirements for nitrification are more demanding than for BOD removal. For instance, 1.5 lb (kg) of oxygen are required to treat 1 lb (kg) of BOD; however, 4.6 lb (kg) of oxygen are required to oxidize 1 lb (kg) of ammonia (NH_3) to nitrate (NO_3^-). Nitrification is accomplished by a set of highly specific microbes referred to as nitrifiers. Biological nitrification is an energy intensive process that can be rather delicate to establish and maintain, because of the nature of nitrifying bacteria. As compared to a facility that does not have to nitrify, electrical energy requirements can be increased by 40 to 50% when nitrification is ongoing.

Be aware that in some cases nitrification is not necessary, yet can be an active process when among other things, solids retention time (SRT) exceeds 3 to 6 days, and oxygen and temperature are adequate. If a facility that is not required to nitrify has some nitrification underway, there can be rather significant yet unnecessary use of energy being consumed for aeration.

Although conversion of ammonia to nitrate is often sufficient from a regulatory point of view, there are instances where nitrogen must be completely removed. This process, called denitrification, can be done both chemically and biologically, and results in nitrogen gas being liberated under the biological approach. In biological denitrification, nitrate (not oxygen) is reduced in a process commonly known as anoxic respiration. Although anoxic respiration does not require the aeration energy necessary to maintain an aerobic environment, it does require high recirculation rates along with an added carbon source, which is often methanol.

One ECM for reducing energy involves creating an anoxic zone, about 15% of total tank volume, at the front of the aeration basin. In this case, BOD is removed anoxically, using nitrate, not aerobically. For facilities with diffused aeration systems, the anoxic zone is facilitated by locally reducing airflow, providing just enough flow for mixing.

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CHAPTER 30

Energy in Cooling Systems

As ambient air temperature increases, many heat-producing processes become cooling limited, making it useful to know the answer to the question "What is the value of one degree colder water?" This value can be difficult to calculate, due to the complexity of some industrial processes. However, the question "What is the cost of one degree warmer water?" may be easier to answer. For instance, a rough answer can sometimes be obtained in the plant's control room. In the middle of a very hot and humid stretch of weather, this statement might be heard: "The cooling water temperature has gone up two degrees; cut production back 10%." The two-degree rise in cooling water temperature can equate to a revenue and profitability loss represented by a 10% process throughput reduction. Therefore, a neglected cooling tower, where thermal performance has decreased, can have adverse consequences on the ability of any plant to achieve revenue and profitability goals.

Financial Impact of Inefficient Heat Rejection

When cooling tower cold water temperature approaches the point where 100% process throughput can no longer be sustained, resourceful process operators try anything to avoid reducing process throughput. Typical strategies include:

- Increase blowdown to introduce more cold makeup water into the system.
- Introduce cold makeup water immediately ahead of a critical heat exchanger.
- Rent portable, temporary cooling towers.

Increased cooling tower blowdown can reduce cooling water supply temperature, if enough makeup water is added to the tower basin water. However, this action reduces the concentration ratio (CR), and may require increased chemical inhibitor feed rate. Adding cooler makeup water before a critical exchanger or adding additional cooling capacity also reduces water temperature of an under-performing cooling system. All of these actions increase the costs of water, discharge, and chemical treatment, ultimately reducing profitability of any facility. Inefficient cooling tower operation can have significant financial consequences on any process operation through increased costs and loss of revenue (Fig. 30.1). Loss of revenue from reduced process throughput is the largest cost resulting from an under-performing cooling tower.

Energy consumption in cooling towers is only due to pumps and fans. Of these, pumps consume the most energy, usually at a constant, year-round rate, except in unusual service conditions. Fans are powered by single-speed motors, two-speed motors, or variable-speed drives and can be operated at reduced speed or shutdown in cooler weather. Under-performing cooling towers require higher fan speed, resulting in increased energy costs. However, these energy cost increases will be small compared with the loss of production efficiency due to decreased tower performance.

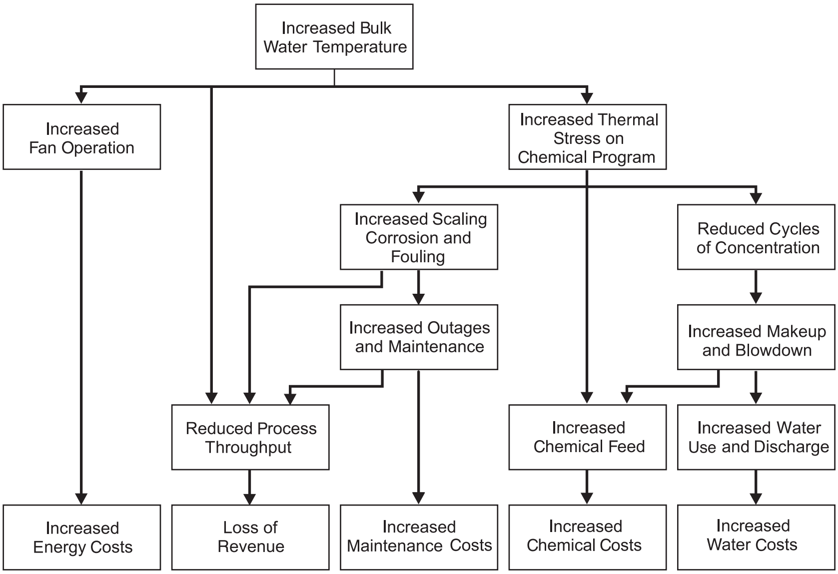


FIGURE 30.1 Consequences of inefficient cooling tower operation. (*Courtesy of Diagnostic Cooling Solutions, Inc.*)

Warmer cooling tower supply and return water, increases thermal stress on the chemical inhibitor program in two areas:

1. Increased fouling, scaling, and microbial growth potential in cooling tower fill (particularly film fill)
2. Increased scaling and corrosion potential in heat exchange equipment

The effect of temperature on deposition and corrosion is covered in Chap. 15 and Chap. 16, respectively.

Each of these problems has serious consequences for both thermal performance and reliability. Normal chemical inhibitors can become less effective in higher temperature situations. If water temperature cannot be reduced, addition of high cost contingency chemical supplements may be required. If scaling and corrosion are not prevented, online cleaning or system shutdown with offline chemical cleaning may be needed. Cooling tower and heat exchanger maintenance costs and the cost of reduced production can be high. Lost production can reach millions of dollars, especially if there is an unplanned outage.

Cooling Tower Thermal Performance or Thermal Capability

The range or delta T (ΔT) of a cooling tower is the temperature drop of the water passing through the tower. The range is the hot return water temperature (T_1), minus cold supply water temperature (T_2), as shown in Eq. (30.1). This ΔT is controlled by the process heat load and is independent of the cooling tower.

$$\Delta T = T_1 - T_2 \tag{30.1}$$

Approach temperature is dictated solely by the cooling tower. The approach temperature (T_A) is the cold water temperature (T_2), minus the ambient wet bulb temperature (T_{WB}), as shown in Eq. (30.2). The approach temperature and cold water temperature are higher than design values in an under-performing cooling tower. However, the approach temperature can often be higher than the design value during normal operation, especially if other system parameters are not at the design values. This is particularly true in colder climates during winter, when the wet-bulb temperature is very low. The range and approach temperature of a tower are represented in Fig. 30.2.

$$T_A = T_2 - T_{WB} \tag{30.2}$$

When cold-water temperature increases to the point that the process is affected, then process throughput must be reduced. Decreased throughput reduces heat load on the cooling tower and therefore reduces ΔT. Thermal performance of the cooling tower may influence the decision to reduce process throughput, and therefore heat load,

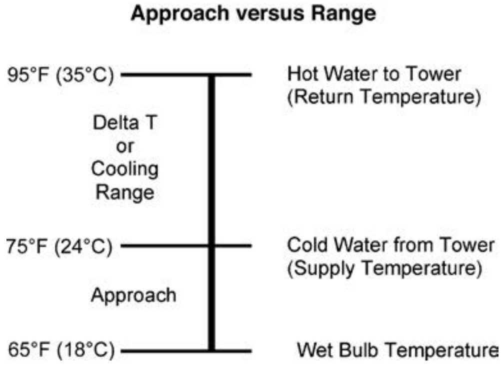


Figure 30.2 Illustration of cooling tower range (ΔT) and approach temperature.

but the cooling tower always accepts whatever heat load is directed to it. Cooling tower thermal performance is the calculated ability of the cooling tower to achieve the design approach temperature, and is expressed as a percentage of the design thermal performance. This cooling tower thermal capability is often referred to as cooling tower efficiency.

Thermal performance of a cooling tower is specified by the cooling tower supplier, at a design operating point defined by hot water temperature, cold water temperature, wet bulb temperature (WBT), water flow rate, and fan power or Liquid/Gas (*L/G*) ratio. Usually, the tower supplier provides the tower owner with a set of performance curves (cold water temperature versus WBT), for a selection of water flow rates and heat loads that bracket the design operating point.

The *L/G* ratio equals the mass of water circulating over the cooling tower divided by the mass of air passing through the cooling tower as shown in Equation 30.3.

$$L/G = R/F_{\text{air}} \tag{30.3}$$

where R = recirculation rate of tower water, lb/min (kg/min)
F_{air} = airflow through tower, lb/min (kg/min)

An example can illustrate the effect of the *L/G* ratio. A system with three fans and three recirculating water pumps has only two fans and two recirculating pumps operating. To obtain colder temperature water from the cooling tower is it better to turn on one more pump or turn on one more fan?

This can be answered easily by looking at the impact of each change using an example of a tower performance curve (Fig. 30.3).

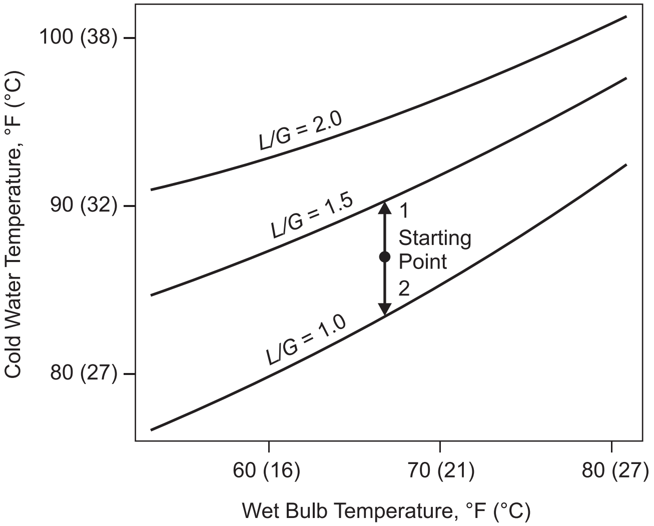


Figure 30.3 Arrows show effect on cold water temperature of increasing (Arrow 1) or decreasing (Arrow 2) *L/G* ratio from a given starting point in a cooling tower.

If water flow is increased, L increases, and the *L/G* ratio increases. From Fig. 30.3, if *L/G* increases at constant WBT, cold water temperature increases, and performance of the system decreases (Arrow 1 in Fig. 30.3). The change shown in Fig. 30.3 would increase cold water temperature about 4°F (2.2°C). However, if airflow is increased, the *L/G* ratio decreases, and cold water temperature decreases at constant WBT (Arrow 2 in Fig. 30.3). This decreases approach to the WBT, and improves tower performance. Arrow 2 shows cold water temperature would decrease about 4°F (2.2°C). Therefore, the correct action is to turn on an additional fan.

Increasing water flow over a cooling tower (increasing *L/G* ratio) decreases cooling tower ΔT and increases cold-water temperature. Increasing airflow through a cooling tower (decreasing *L/G* ratio) does not affect ΔT but decreases cold-water temperature.

In multi-cell cooling towers, the *L/G* ratio for individual tower cells should not vary widely from cell to cell, otherwise thermal performance is degraded. Ideally, each cell of a four-cell cooling tower would use 25% of the total fan power, deliver 25% of the total airflow, and reject 25% of the total heat, while using 25% of the total water flow.

However, multi-cell towers are not usually perfectly balanced in the real world. A thorough mechanical survey of a multi-cell cooling tower can identify under-performing cells and determine the nature of the problem. A performance grade can be assigned for each cell for

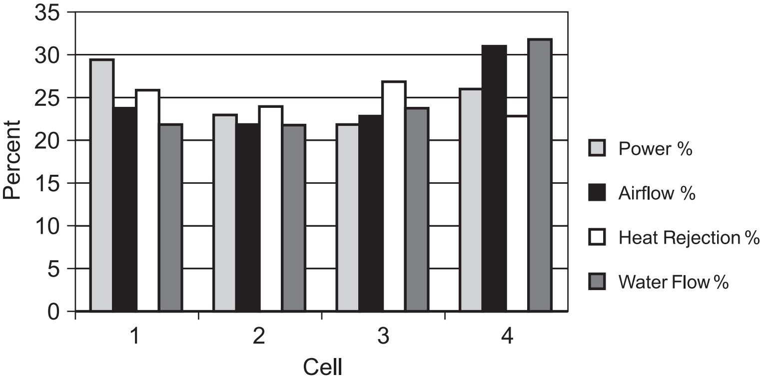


Figure 30.4 Typical cooling tower cell performance distribution illustrating uneven loading and heat rejection. (*Courtesy of Diagnostic Cooling Solutions, Inc.*)

the purpose of prioritizing and scheduling planned maintenance activities.

Figure 30.4 shows an airflow problem in Cell 1, because the percent power is significantly greater than the percent airflow. Plugged or fouled fill or drift eliminators, excessive air leakage at the fan blade tips or fan hub, or fan stall (described later) could cause reduced airflow. An exit air velocity profile can be used to identify the precise cause.

Figure 30.4 also shows a thermal problem in Cell 4, as percent heat rejection is significantly lower than either percent airflow or percent water flow. Poor air/water contact from distribution or channeling problems can cause this, and nozzle spray patterns and fill condition should be checked. Cells 2 and 3 are giving satisfactory thermal performance and need no attention.

By identifying problem cells and the nature of the problems, maintenance can be prioritized and scheduled to maximize thermal performance. Downtime and maintenance costs can be minimized by delaying repairs with lower thermal performance benefit, and by avoiding unnecessary maintenance on cells that provide satisfactory thermal performance. This technique is particularly useful when planning for plant shutdown, where budgets and available repair time are tightly controlled.

As indicated in Fig. 30.4, some situations can be positive. Higher percent heat rejection than percent airflow in Cell 1 can indicate good contact between water and air in that cell. Similarly, percent heat rejection that is greater than percent water flow can indicate good air/water distribution and good contact. Table 30.1 shows some of the problems, causes, and possible points to inspect in a tower for the situations shown in Fig. 30.4. Several of the inspection items fit several situations.

Situation	Possible Causes	Inspection Items
% Airflow exceeds % Power input	Possible air or water channeling Low water flow in cell compared to other cells	Broken fill Irregular spray pattern from nozzles Uneven water flow across cell Plugged nozzles Deck water level not balanced between cells in crossflow tower.
% Power input exceeds % Airflow	High water flow in cell Fan air leakage Fan over or under pitching Obstructions to airflow Fan inlet spin	Flooded fill in cell Excessive fan blade tip clearance Hub disk broken or missing Poor exit air velocity profile Plugged or fouled fill in cell Vortex or spin of plume in plenum
% Airflow exceeds % Heat rejection	Poor air/water contact Possible air or water channeling	Broken fill Irregular spray pattern from nozzles Plugged nozzles
% Water flow exceeds % Heat rejection	Poor air/water contact Poor water distribution Possible air or water channeling	Flooded fill in cell Uneven water flow across cell Deck water level too high in cell in crossflow tower. Excessive water flow in spray header in counterflow tower.

Table 30.1 Example Causes of Imbalances in Power Use, Heat Rejection, Water Flow, and Airflow between Cells in a Cooling Tower

Cooling Tower Performance Problems

An under-performing cooling tower confronts the tower operator with a variety of choices to fix the system. The most common repairs performed on cooling towers are fill and nozzle replacement. However, these repairs may not solve the basic performance problem, if a thorough mechanical survey with performance testing of the system has not been undertaken. The basics of a complete Mechanical-Operational-Chemical (MOC) audit were described in Chap. 14. Repairs that do not address the root causes of the performance problem waste the maintenance budget and possibly result in further deterioration in thermal performance of the cooling tower.

Excluding safety, health, and environmental issues, common cooling tower performance related problems can be categorized in four ways:

1. Air-side thermal performance issues
2. Water-side thermal performance issues
3. Energy
4. Reliability

Air-Side Thermal Performance Issues

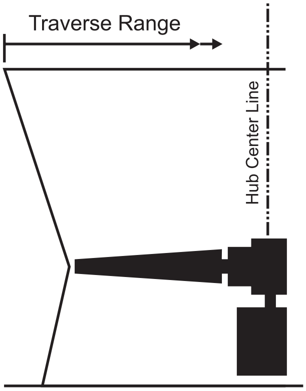
Airflow problems are usually more difficult to identify than water flow problems. Water flow is easier to measure than airflow, and flow variation or water channeling in tower fill can be visually observed. One method of analyzing airflow requires plotting results of multiple radial air velocity measurements of the fan cylinder exhaust plane (Fig. 30.5) to generate a profile of exit air velocity along the radius of the fan stack.

An in-service field test on a tapered-blade fan, installed in a properly operating cooling tower, would produce a radial exit air velocity profile similar to Fig. 30.6. Maximum air velocity occurs at mid-blade. Deviations from the ideal profile can reveal a variety of problems such as excessive blade tip clearance, hub seal disc leakage, blade deposits or pitting, airflow obstructions, fan blade aerodynamic stall, or under pitching. This enables the tower operator to target the most urgent problems with minimum delay and expense. Figure 30.7 indicates average airflow improvement opportunities for various problems of fan operation, which are described in more detail below.

Blade Pitch

The pitch or angle of attack of a variable-pitch fan blade can affect airflow through the tower. Loss of lift on airplane wings, which causes the plane to stall, is a similar effect. When the angle of an airplane wing relative to the incoming wind (angle of attack) is too steep, airflow separates from the top of the wing, increasing drag and turbulence, causing a loss of lift. An angle of attack that is too small also reduces lift. An angle

Figure 30.5 Exhaust plane velocity traverse. (*Courtesy of Diagnostic Cooling Solutions, Inc.*)



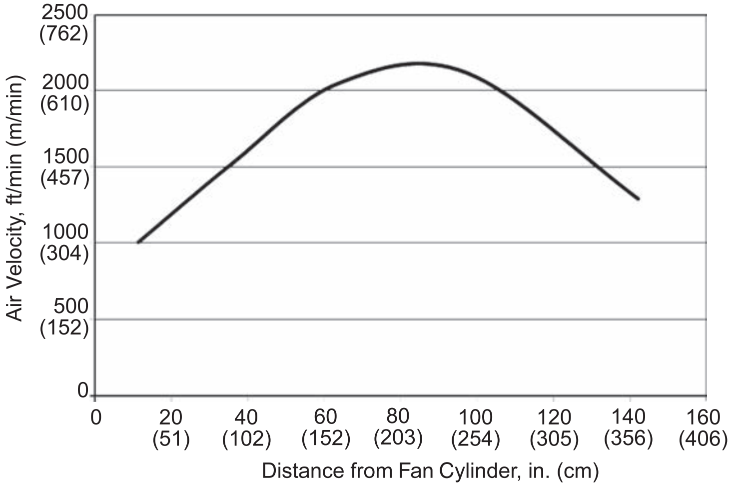


Figure 30.6 Normal exit air velocity profile along radius of fan stack. (*Courtesy of Diagnostic Cooling Solutions, Inc.*)

of attack that is too low in a tower fan blade is often called under pitching and an angle of attack that is too high is called over pitching (Fig. 30.8).

Under pitching cooling tower fan blades reduces airflow created by the fan. Over pitching fan blades increases blade turbulence and drag, also reducing airflow. Like an airplane wing, over pitching is known as fan stall and cannot be detected from fan motor power measurements. Once the stall point is exceeded, increasing blade pitch reduces airflow, while increasing fan motor power due to

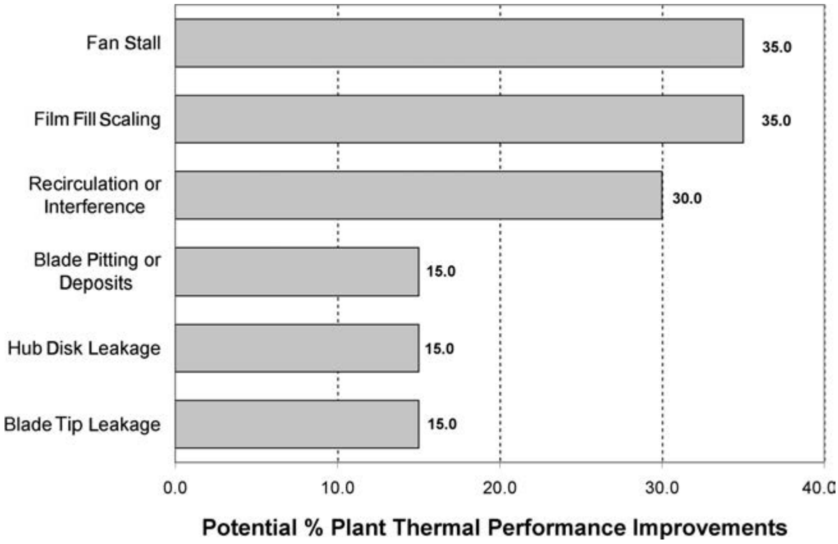


Figure 30.7 Air-side improvement opportunities.

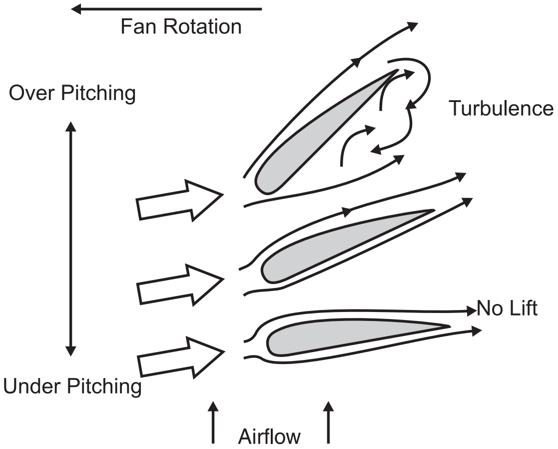


Figure 30.8 Illustration of fan stall from excessive angle of attack.

increased drag. Fan stall can also be caused by throttled airflow and high altitude. Fan stall has a significant adverse effect on cooling tower thermal performance. Reduced airflow through cooling tower fill from either condition increases the *L/G* ratio and the approach temperature, reducing tower thermal performance.

Fan Leakage

Air leakage around or into the fan suction side can reduce airflow and tower performance (Fig. 30.9). Fan leakage occurs from two main causes:

1. Air leaking from the high-pressure side of the fan to the low-pressure side, either at the blade tip or at the hub

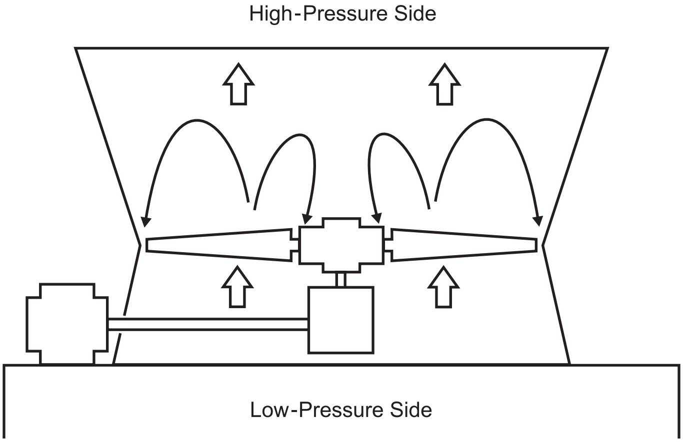


Figure 30.9 Potential locations of air leakage around cooling tower fan.

Figure 30.10 Air leakage can occur through holes and gaps in the fan stack.

2. Air leaking into the fan cylinder at holes or gaps in the fan stack, such as where the motor shaft goes through the fan cylinder (Fig. 30.10)

Excessive blade tip clearance results in air leakage between the blade tip and fan cylinder. Poorly designed, broken, or missing hub discs result in air leakage through the hub. Hub discs are installed to control air passing through the hub area of the fan. Some hub designs, for example, spoke designs, are more prone to leakage. Figure 30.11 shows a fan with a hub disk installed.

Figure 30.11 Fan with a hub disk installed to prevent air leakage from the high-pressure to the low-pressure side of the fan. (*Courtesy of SPX Cooling Technologies, Inc*.)

Blade Condition

Blade wear typically occurs in the form of pitting from droplets of water entrained in the airflow (called drift). This pitting initially occurs at the highest air velocity point on the blade. Blade wear or deposits create turbulence, disrupt airflow over the blade airfoil, and increase drag, resulting in reduced airflow and increased fan power requirement.

Plenum Spin/Fan Inlet Spin

When fans are tested in a laboratory wind tunnel, airflow straighteners are often installed directly upstream of the fan being tested to achieve maximum performance. Absence of airflow straighteners in normal cooling towers may cause air in the fan inlet to spin as it approaches the fan. This is known as fan inlet spin or fan inlet swirl (Fig. 30.12). Rotation of air can occur in the plenum too. This produces the same effect as an aircraft losing lift if it was to try to take off going with the wind. For example, a fan could be designed to rotate at 100 rpm. If air in the fan inlet spins at 10 rpm as it approaches the fan, the effective speed of the fan is reduced to 90 rpm. Actual airflow will be 10% less than design, because fan airflow is directly proportional to fan speed. Increasing fan blade pitch to compensate can offset this reduced airflow, but may create a fan stall condition, which is much worse.

Air Channeling

Flowing air always takes the path of least resistance, for example, where tower fill is broken or missing or where lowest water flow exists. Air that bypasses contact with water compounds the adverse effect of water channeling on thermal performance of the tower.

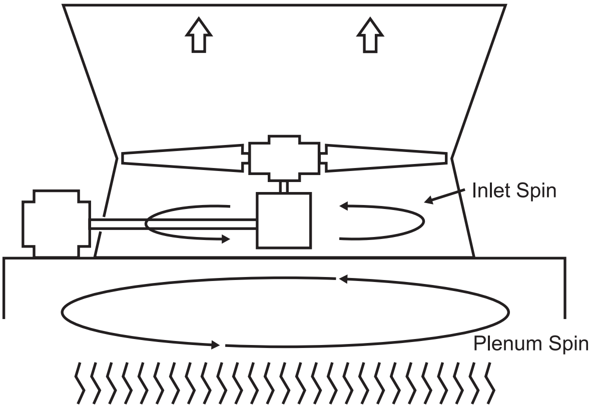


FIGURE 30.12 Illustration of inlet and plenum spin induced in air entering fan stack.

Air Velocity

High air velocity, whether resulting from poor design, air channeling, or obstructions can cause various problems in different parts of the tower. For instance, excessive airflow velocity in film fill can result in cooling water evaporating to dryness in the fill pack, causing scaling that can progress at an alarming rate.

Cell Balancing

For optimum thermal performance, airflow needs to be equally distributed among cells to maintain design *L/G* ratio. This was illustrated earlier in Fig. 30.4.

Recirculation and Interference

Recirculation occurs when cooling tower inlet air is adulterated by exit air from the same cooling tower. Interference is when cooling tower inlet air is adulterated by exit air from an adjacent cooling tower or warm or moist air from another source (Fig. 30.13). While some cooling tower designs are more prone to recirculation and interference, other factors such as location, orientation, and wind direction have significant impact.

Water-Side Thermal Performance Issues

Water flow and airflow must be uniform throughout the tower to achieve optimum cooling tower thermal performance. On crossflow cooling towers, water flow on the tower deck should be balanced between each cell or each side of a cell. As airflow takes the path of least resistance, air is preferentially drawn through the side of the cell with the least water flow, reducing thermal performance efficiency. This can be caused by different water levels in the water distribution deck of different cells, or different sides of the same cell, as shown in Fig. 30.14. The lower water level on the right side of the deck reduces water flow and increases airflow through that side of the cell.

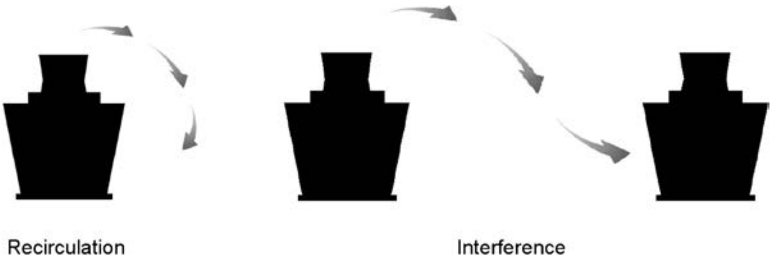


FIGURE 30.13 Recirculation and interference. (*Courtesy of Diagnostic Cooling Solutions, Inc.*)

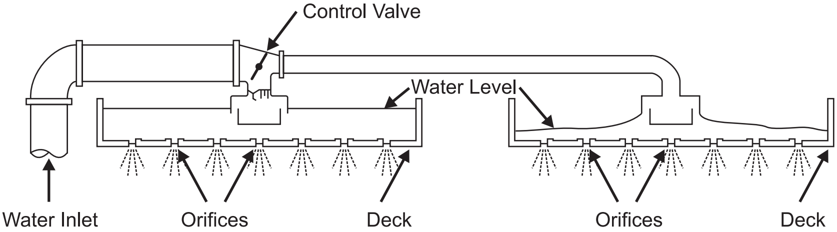


FIGURE 30.14 Water level on the deck of a crossflow cooling tower can affect water flow and airflow through each part of the tower. The section of fill under the deck on the right may have insufficient water flow.

Measurements of water flow in a crossflow cooling tower (Fig. 30.15) illustrate this point by showing how airflow can be different between cells, or between different sides of the same tower cell. Although Cells 3 and 4 have the same total water flow, one side of each cell has double the flow of the other side. Performance loss from this water-side channeling is compounded by airflow channeling that also occurs in these cells. Water flows over each side of Cells 1 and 2 are balanced, but Cell 1 has double the flow of Cell 2. Higher *L/G* ratio in Cell 1 can reduce thermal performance. Analysis of individual cell flows and deck water levels are useful in comparing fill water loadings with design values.

Fill Water Loading

Both high and low fill water loadings can cause performance and reliability problems. For optimum thermal performance, water flow needs to be equally distributed among cells to maintain the designed *L/G* ratio. Channeling or nonuniform water flow through fill causes preferential air channeling through fill areas where there is the least water. This reduced contact between water and air, reduces evaporation and

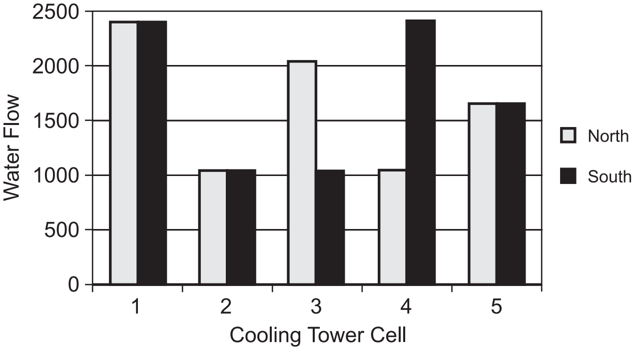


FIGURE 30.15 Water flow on a multi-cell crossflow cooling tower. (*Courtesy of Diagnostic Cooling Solutions, Inc.*)

tower performance. Excessive water loading of film fill can hold back airflow, until the air finally percolates through the increased amount of water. Insufficient water loading on any part of a film fill pack results in evaporation to dryness and progressive scaling of the fill.

Film Fill Scaling

In addition to low water loading that causes dryness in the fill, scaling in tower fill can occur from a number of causes. Other causes can include high temperature stress, low inhibitor dosage, or even rapid carbon dioxide stripping from water in the tower fill. As scale thickness increases in film fill, the fill pack becomes progressively heavier due to the combined weight of scale and additional water. This may continue to the point where the support system fails, and fill falls into the basin.

Water Bypassing Fill

There are a variety of causes of water channeling in crossflow and counterflow cooling towers. Some spray from perimeter nozzles is often directed down cell partitions, bypassing fill and avoiding contact with air. This can be kept to a minimum by installing deflectors to redirect water back onto the fill. Broken or plugged spray nozzles can affect water flow in either type of tower (Fig. 30.16). A broken nozzle, or one with a broken splash or spray bar, may not spread water properly over fill. The fill under a plugged nozzle has little or no water flow. In a counterflow tower, low system water pressure in the distribution header for spray nozzles can reduce water flow for an entire cell.

Cooling Tower Energy Balance

The ever-increasing cost of energy is driving the need for efficient process operations. A mechanical audit of the cooling tower, including testing to evaluate tower performance, can provide vital information enabling the tower operator to compare operating costs to design values.

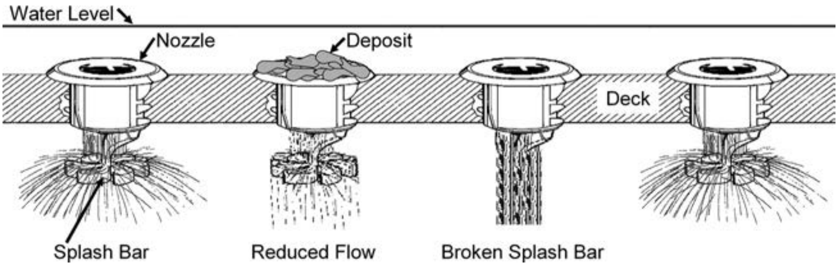


Figure 30.16 Examples of spray nozzle problems in a crossflow tower that can cause water channeling.

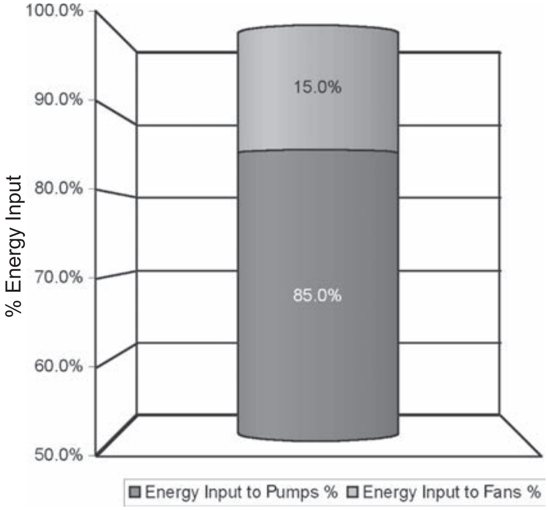


Figure 30.17 Energy consumption in a cooling tower system.

Typically, cooling tower operating energy is 2 to 6% of total energy (heat rejection plus operating energy equals total energy). These estimates vary with climate, tower design, plant layout, and cooling duty. Pump energy consumption is approximately 85% of total operating energy, depending on tower design and plant layout. Figure 30.17 shows the typical breakdown of energy usage by cooling tower equipment. Performance of pumps and fans should be maintained at peak levels to maintain efficiency. However, thermal energy rejected by the cooling tower should be the focus of efforts to maintain performance of the entire system.

A mechanical audit of the tower to evaluate performance should collect a wide variety of inputs, including flow and temperature data. Typical data for water and airflow are shown in Fig. 30.18. Other data, like the fan exit air velocity profile and inspection points described in this chapter, should be part of a complete mechanical survey of a cooling tower. The data in Fig. 30.18 can be used to calculate the *L*/*G* ratio and heat balance. A variety of other tower characteristics like CR of the water can be determined using equations in Chap. 14.

The *L*/*G* ratio and approach temperature are two of the more important data points that can be determined from this input data. If either water or airflow changes, then the *L*/*G* ratio changes. As described earlier in this chapter, a decrease in *L*/*G* ratio reduces approach temperature and cold water temperature of the tower. The opposite happens if water flow increases, causing an increase of *L*/*G* ratio. While airflow is more difficult to measure, water and air temperatures can be measured easily. Changes of approach temperature

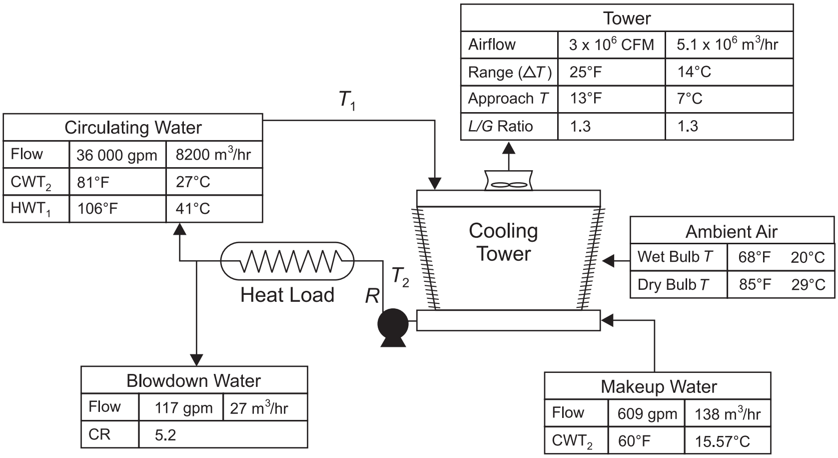


Figure 30.18 Inputs and outputs from a cooling tower that can be used to calculate performance and energy balance.

and range (Δ*T*) of the cooling tower can signal that something else has changed. Many things can affect these two parameters. A detailed analysis of a complete mechanical audit of the tower performance would be needed to determine the root cause of a change in approach temperature or Δ*T*.

For example, if Δ*T* of the tower decreases, two of the possible causes are, a drop in heat load from the process or an increase in water flow, which increases the *L/G* ratio. Change in airflow does not affect Δ*T*. If approach temperature increases, possible causes include, an increase in heat load or water flow increase (*L/G* ratio increases). Approach temperature would also increase if ambient air humidity increases. Thus, it is necessary to have a complete set of information in order to assess tower performance.

Reliability Issues

In a cooling tower, reliability issues can involve everything from structure to mechanical equipment to water treatment. Structural issues are outside the scope of this chapter, and water treatment issues are covered elsewhere in this book. The most critical mechanical equipment is fans, pumps, and their respective motors. Premature or unexpected failure can result in reduced cooling capability, at best causing reduced process throughput or at worst an unplanned outage.

Fan and Pump Motor Reliability

Power supply quality and current draw are indicators of the health of a pump or fan motor. For instance, an extreme case of phase voltage unbalance can reduce expected life of a fan motor from 20 years to 9 months.

Fan Vibration

Fan vibration is an indicator of an unbalanced fan or drive shaft. Vibration that continues or worsens may result in fatigue failure of a coupling, drive shaft, gearbox, or fan blade, ultimately destroying the fan.

Pump Cavitation

Cavitation is the implosion of vapor voids or bubbles in water due to rapid localized changes in pressure (Fig. 30.19). This can be caused by low pump suction pressure. Cavitation erosion of pump internals can be very severe, and pump flow declines as impeller erosion progresses.

Inefficiency in Older Cooling Towers

Continuing improvements in design of cooling towers and their component parts has resulted in reduced cooling tower size and increased reliability. Components that are particularly noteworthy are nozzles, fill, and drift eliminators. Counterflow cooling tower nozzles now produce much more even spray patterns and are more reliable than older versions. Film fill is now available for a range of water qualities and for applications from comfort cooling to industrial production. Due to additives in the plastic, film fill life expectancy is significantly longer. Cellular drift eliminators can now limit drift to 0.0005% of the recirculating rate, while maintaining satisfactory static pressure drop. As a result, older cooling towers not equipped with these newer design components can suffer greater thermal loss from under performance.

The causes of thermal performance, energy wastage, and reliability problems that have been presented in this chapter are summarized in

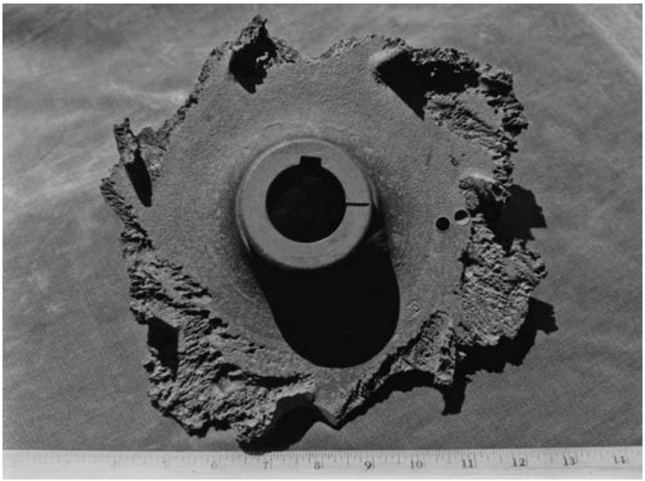


Figure 30.19 Cavitation damage on pump impeller.

Common Cooling Tower Problems			
Air-Side Problems	**Thermal Performance**	**Energy**	**Reliability**
Hub disc leakage	X	X	
Blade tip leakage (excessive blade tip clearance)	X	X	
Blade under pitching	X		
Fan stall (blade over pitching)	X	X	
Blade wear/pitting	X	X	X
Fan vibration			X
Fan motor power supply		X	X
Cell-to-cell airflow balance	X	X	
Plenum/fan inlet spin	X	X	
Water-Side Problems			
Cell-to-cell water flow balance	X	X	
Water by-passing fill	X	X	
Fill water loading	X	X	X
Film fill scaling	X	X	X
Recirculation or interference	X	X	
Channeling	X	X	
Pump cavitation		X	X

Courtesy of Diagnostic Cooling Solutions, Inc.

Table 30.2 Summary of Common Cooling Tower Problems and Impact on Performance

Table 30.2. Many of these problems can only be found by inspection or by specialized test measurements of a system. These should be undertaken during a complete mechanical audit of the cooling system that measures performance of key cooling tower parameters.

Cooling Tower Performance Testing

The dilemma of deciding what repairs to undertake with a limited repair budget has resulted in wider use of cooling tower testing to verify contractual thermal performance, and to diagnose root causes of problems.

Early cooling tower performance curves were published in 1943. The Cooling Technology Institute (CTI) (formerly Cooling Tower Institute) published the most comprehensive book of cooling tower characteristic charts in 1967. These charts were used to size a cooling tower for a specific process heat load, and to enable cooling tower thermal performance to be checked against design specifications. These performance calculations and comparisons are now totally computerized. The CTI also publishes the Cooling Tower Acceptance Test Code, for contractual thermal performance verification of new and refurbished cooling towers. CTI reports annually on results of cooling towers that have been tested in accordance with the code.

Cooling Tower Acceptance Testing

The CTI test code provides acceptance test procedures for various tower types. There are two basic test methods: the performance curve method and characteristic curve method. Both methods require specialized testing equipment for data collection. Because measured values of hot water temperature, cold water temperature, WBT, water flow rate, fan power, and *L/G* ratio are not likely to match design values, calculations of performance and corrections can be complex. Therefore, an experienced individual is recommended to carry out testing and analysis.

The main purpose of the CTI Acceptance Test Code is to verify contractual performance guarantees of a new or refurbished cooling tower. The test can be used to compare current cooling tower thermal performance to the original, repaired, or contractual performance guarantee. During the test, cooling tower operating conditions such as recirculation and interference can degrade cooling tower thermal performance. Because these factors are outside of the control of the cooling tower supplier or repair contractor, the CTI Acceptance Test Code is designed to exclude effects of recirculation and interference from the performance test. As a result, cooling tower thermal performance as determined by the CTI Acceptance Test can exceed actual performance experienced with a cooling tower, if recirculation or interference is occurring.

Where thermal performance is in question, the CTI Acceptance Test Code has often been used as one method to check the status of older cooling towers. However, because the CTI Acceptance Test does not have specific diagnostic capabilities, it usually can only verify that the cooling tower is under performing, as was previously suspected, without determining why.

Cooling Tower Performance Audit

Diagnostic performance testing of a cooling tower as part of a complete MOC system survey can help find the root cause of tower performance problems. The mechanical portion of the survey should collect current and design operating parameters for the cooling tower system. Basic calculations that define dynamics of a cooling tower are described in Chap. 14. Test methods to evaluate performance of fans, pumps, water flow, airflow, etc. require specialized equipment, procedures, and knowledge. An individual who is trained for this type of testing should perform the audit. Typical goals of diagnostic testing include:

- To troubleshoot and restore cooling tower thermal performance
- To predict cooling tower thermal performance at alternative operating conditions, such as various water flows or heat loads
- To upgrade cooling tower thermal performance to accommodate process changes or plant expansion
- To identify, target, and prioritize needed repairs within each cell
- To identify and prioritize repairs before a planned plant shutdown, so that sufficient maintenance time and budget can be allocated
- To monitor cooling tower film fill thermal performance

Diagnostic testing has the advantage of being carried out on an operating cooling tower, whereas an inspection requires a planned outage. Thermal performance impact of identified problems can be determined when the cooling tower is in operation, and can help prioritize necessary repairs. For instance, in the case of a planned cell-by-cell refurbish of a multi-cell cooling tower, a diagnostic test can define the order in which cells should be restored for optimum thermal performance.

The capability to identify obscure problems can be important on large multi-cell cooling towers, where blanket or random repairs would involve excessive downtime and expense with no guarantee of success. Examples of information that would be beneficial to obtain during a performance audit include:

- Cell water flow balance
- Fan motor diagnostics
- Fan stall
- Fan inlet/plenum spin
- Cell fan power, airflow, and heat rejection balance
- Cell fan and pump operating energy balance
- Cell operating energy efficiency

The ability of diagnostic testing procedures to detect and isolate performance problems, particularly obscure problems, can be beneficial in maximizing the value contribution of a cooling tower to the entire production process.

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CHAPTER 31

Energy in Steam Systems

Energy is the largest part of a facility's costs associated with the generation of steam, that is, fuel, water, chemicals, labor, and maintenance. Typically, 60 to 70% or more of the cost of steam comes directly from the fuel consumed. By comparison, 5% can be attributed to the cost of water, and typically, less than 3% is from water treatment costs. Since fuel is the largest cost, it is obvious that any improvement that directly saves energy, and thus fuel, is of great interest.

Recent studies of industrial boiler/steam generation plants show significant opportunities exist to reduce energy wastage and fuel consumption. Beginning in fiscal year 2006, the U.S. Department of Energy (DOE) started an industrial assessment campaign, which involved the largest energy-consuming manufacturing plants in the United States. Trained assessment teams identified and evaluated promising opportunities in a site's steam system for the ability to cut energy use and reduce carbon emissions. Results of the top 10 steam saving opportunities for the first 114 steam assessments are shown in Fig. 31.1. This useful checklist provides key energy saving project areas or opportunities for many plants.

Energy Basics for Steam Systems

As heat is supplied to water, the temperature increases until boiling occurs at 212°F (100°C) under atmospheric pressure. At the boiling point, the temperature remains constant until all the water is converted to vapor. The specific heat of water is 1 Btu/[lb · °F] (4.184 kJ/[kg · °C]), and 152 Btu/lb (353 kJ/kg) is needed to raise the temperature of water from 60°F (15.6°C) to 212°F (100°C). In contrast, the heat of vaporization for water at 212°F (100°C) is 970 Btu/lb (2256 kJ/kg) to change water to steam. Therefore, about six times more energy is needed to evaporate water at the atmospheric boiling point than to heat the water from 60°F (15.6°C) to 212°F (100°C).

If the pressure of the water is increased, as it is in a boiler, the boiling point also increases, requiring the application of still more heat to

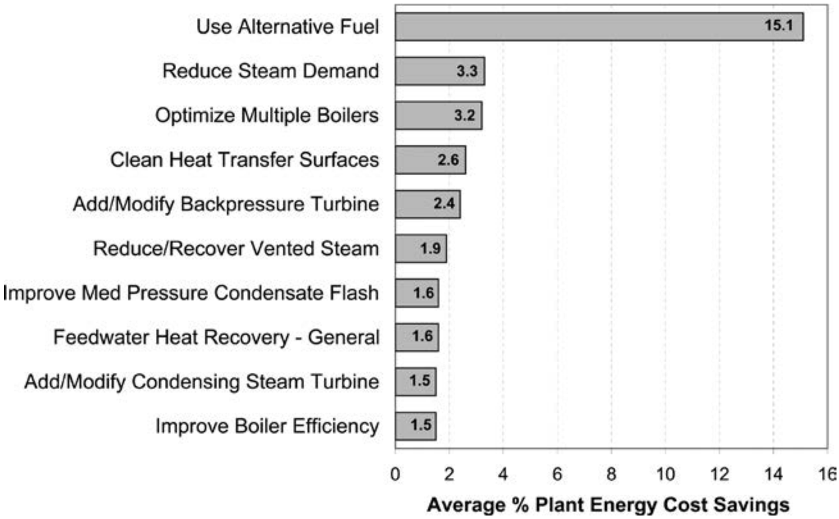


Figure 31.1 Top 10 steam savings opportunities. (*Source: Data compiled from ORNL/TM-2007/138.*)

raise the temperature and vaporize the water. Steam at higher pressure, then, has a higher temperature and contains more energy than steam at atmospheric pressure. Another important change is the reduction in volume as the pressure increases.

Steam tables have been developed to relate these properties of steam and water at various temperatures and pressures. Table 31.1 illustrates some of the information found in steam tables. A complete discussion of steam tables is beyond the scope of this book, but some basic orientation is necessary for understanding power generation processes.

Enthalpy

The term enthalpy denotes the heat content of a substance, expressed in Btu/lb (kJ/kg). It is most typically represented by the symbols *H* or *h*. Since water changes from liquid to solid below 32°F (0°C) at atmospheric pressure, this discussion is limited to higher temperatures.

Temperature		Absolute Pressure		Liquid Enthalpy		Vapor Enthalpy	
°F	°C	psia	kPaa	Btu/lb	kJ/kg	Btu/lb	kJ/kg
60	15.6	0.256	1.765	28.040	65.192	1087.8	2529.0
120	48.9	1.693	11.673	87.976	204.54	1113.6	2589.1
180	82.2	7.512	51.796	147.99	344.08	1138.2	2646.3
240	115.6	24.965	172.12	208.46	484.66	1160.6	2698.5
300	148.9	66.993	461.90	269.74	627.13	1179.8	2742.9

Table 31.1 Saturated Steam Table Example

In discussing energy, the heat content of water and steam, as well as the amount of energy added, must be calculated. The change in energy needs based on potential energy saving projects, and how this translates into energy costs or savings must also be calculated.

Here is a simple example. How much energy is required to raise the temperature of water in a heat exchanger from 60 to 120°F (15.6–48.9°C) when the water flow is 100 gpm (22.7 m^3/h)?

Steam tables can be used to determine the enthalpy of water at 60°F (15.6°C) and 120°F (48.9°C). From Table 31.1, the values are 28 and 88 Btu/lb (65 and 205 kJ/kg), respectively. The difference in enthalpy is 60 Btu/lb (140 kJ/kg). To find the rate of energy addition to heat the water in this example, the calculation is:

$$(60\ \text{Btu/lb})(100\ \text{gpm})(8.33\ \text{lb/gal}) = 49\,980\ \text{Btu/min}$$

$$(140\ \text{kJ/kg})(22.7\ \text{m}^3\text{/h})(1000\ \text{kg/m}^3)(1\ \text{h}/60\ \text{min}) = 52\,970\ \text{kJ/min}$$

Steam Quality

The terms saturated, dry, and moist are often used in describing steam. What the steam tables call saturated steam could also be called dry and saturated. In other words, it is vapor in equilibrium with water at the boiling temperature, containing no liquid. Steam that contains water droplets is called wet steam. Steam issuing from the spout of the teakettle on the stove is colorless or invisible, just as it leaves the spout; this is dry saturated steam. A short distance from the spout it turns white. This "cloudy steam" contains less heat per pound (kilogram) and is wet steam, because some of the vapor has given up its heat and condensed into tiny droplets of water.

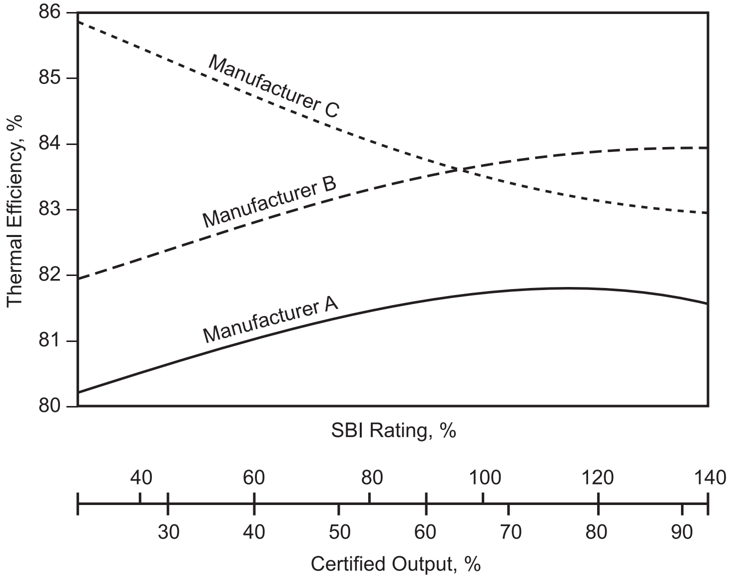
Wet steam always has less heat per pound (kilogram) than dry steam; consequently, it does less work. The term quality is often used to denote the dryness of steam: 100% quality means dry and 90% quality means the steam contains 10% moisture by weight.

After vaporization, additional heat may be added to the steam, increasing its temperature and energy; this is called superheated steam. Superheating not only increases the energy content, but also permits transporting the steam through pipelines with less condensation. Condensation decreases the efficiency of heat engines (turbines) and causes heat loss and water hammer in steam lines.

Boiler Efficiency

In most plants, the operation of a boiler system consumes more energy than any other area of the plant, and for this reason, it is very important that the boilers operate efficiently. Typically, the economic impact of any boiler-related changes is quantified in terms of changes in boiler efficiency. However, before discussing boiler efficiency, it is necessary to first discuss the relationships between capacity and efficiency.

Like many other types of mechanical equipment, boilers are expected to operate over a wide range of capacities or steaming rates. Because the



Certified test by manufacturer

FIGURE 31.2 Typical packaged watertube boiler performance curves.

efficiency of a boiler varies with the boiler steaming (firing) rate, a single arbitrary rating is not only meaningless but also apt to be misleading. For the proper analysis of the operational characteristics of a boiler installation, it is necessary to have performance curves. Figure 31.2 shows typical performance curves for packaged watertube boilers.

The measure of the ability of a boiler to transfer heat from the furnace to the water and steam is its boiler efficiency. This typically takes into account the furnace, superheater, reheater, economizer, and air preheater. In measuring efficiency, it is not usually practical to separate burner (or grate), furnace, and boiler efficiencies. The efficiency of a boiler is considered the combined efficiency of all its elements and is generally expressed as a percentage figure.

The determination of the efficiency of a boiler is in reality a performance test. On large installations, such tests are conducted during actual operation; smaller boilers are tested either in the laboratory or in the field under semi-controlled conditions. There are many ways to track boiler efficiency; some methods are quite complex, requiring special tools to measure the efficiency.

The average efficiency of a boiler and burner installation will vary based on operating conditions. The determination of the maximum attainable efficiency depends on the following:

- Boiler design, including heating surface arrangement and effectiveness of direct and indirect surface placement; furnace volume and shape; combustion product flow through the boiler passes; and water and steam circulation within the boiler

- Built-in losses, such as heat transfer through boiler walls and setting, and irrecoverable flue gas and ash heat losses
- Built-in heat recovery equipment, such as air preheaters, economizers, and blowdown heat recovery systems
- Type of fuel burned and its inherent characteristics
- Rate of firing in relation to furnace volume and heating surface
- Controllability of the variable conditions

In any given installation, boiler efficiency will vary from hour to hour, day to day, and season to season, depending on the following variable conditions:

- Condition of the fuel when fired
- Draft as affected by barometric pressure
- Burner adjustment
- Percentage of excess air
- Cleanliness of heat absorbing surfaces
- Rate of firing
- Temperature and humidity of combustion air
- Incompleteness of combustion or unburned carbon
- Type of operation, whether continuous or intermittent, on–off, high–low, or modulating

Therefore, boiler efficiency is not a static value for a given boiler installation but rather is constantly changing with operating conditions. This is important to remember for two reasons:

1. It is not necessary to spend great time and money to obtain an exact value for boiler efficiency. Simple calculations and rules-of-thumb are probably adequate to evaluate and justify energy saving projects.
2. The change in boiler efficiency due to energy saving projects is the important concept to capture in cost saving calculations, not the absolute boiler efficiency itself.

Boiler efficiency is important, because this value is used in economic calculations for energy saving projects and evaluations. When calculating the potential cost savings for steam system projects [blowdown heat recovery equipment, increased cycles of concentration (COC), increased steam condensate recovery, etc.], the boiler efficiency is used to translate the potential heat or energy savings to fuel savings, which can then be expressed in monetary terms.

Anyone planning to conduct boiler efficiency measurements is encouraged to read the U.S. DOE Steam System Survey Guide (ORNL/TM-2001/263). The rigorous methods to conduct boiler efficiency tests and calculations are described in the American Society of Mechanical Engineers (ASME) Power Test Code (PTC) 4.1, Steam Generating Units.

Definitions

Before calculating boiler efficiency, a number of terms and measurements need to be understood. The following are the important ones to obtain a valid result for boiler efficiency.

Combustion Efficiency

Combustion efficiency is similar to boiler efficiency, with shell, blowdown, and miscellaneous losses omitted. It is expressed as a percentage of total fuel input energy.

Combustion efficiency is an indication of the burner's ability to burn fuel. The amount of unburned fuel and excess air in the exhaust are used to assess a burner's combustion efficiency. Burners resulting in low levels of unburned fuel, while operating at low excess air levels, are considered efficient. Well-designed burners firing gaseous and liquid fuels operate at excess air levels of 15% and result in negligible unburned fuel. By operating at only 15% excess air, less heat from the combustion process is used to heat the combustion air, which increases the heat available to generate steam.

Combustion efficiency is not the same for all fuels. Gaseous and liquid fuels burn more completely than solid fuels, but some fuels, such as natural gas, lose a portion of the fuel energy up the stack with the water vapor formed during combustion. Table 31.2 shows typical combustion efficiency by fuel type.

Boiler Efficiency

The term boiler efficiency is often used interchangeably with the terms thermal efficiency or fuel-to-steam efficiency. Where the term boiler efficiency is used, it is important to know which type of efficiency is being represented, because thermal efficiency, which does

Fuel Type	Fuel	Efficiency (%)
Solid	Coal	89
	Wood	74
Liquid	No. 2 Oil	88
	No. 6 Oil	88
Gas	Natural Gas	85

Table 31.2 Typical Combustion Efficiency by Fuel Type

not account for radiation and convection losses, is not an indication of the true boiler efficiency. Fuel-to-steam efficiency, which does account for radiation and convection losses, is a true indication of overall boiler efficiency. The term boiler efficiency should be defined and understood before it is used in any economic evaluation.

Fuel-to-Steam Efficiency

This is a measure of the overall boiler efficiency, including radiation and convection losses, ambient air temperature, burner efficiency, and fuel type. This should take into account the effects of an economizer and air preheater. It is an indication of the true boiler efficiency and should be the efficiency number used in economic evaluations. The fuel-to-steam efficiency may also be called boiler efficiency or total thermal efficiency.

As prescribed by the ASME PTC 4.1, Steam Generating Units, and the actual fuel-to-steam efficiency can be determined in two ways:

1. Input–output or direct method
2. Heat loss or indirect method

Input–Output or Direct Method

Commonly called the direct method; this value is calculated by dividing the boiler steam output, by the boiler fuel input, and multiplying by 100. This measurement provides a snapshot boiler efficiency, given accurate input and output rates. The actual input and output of the boiler are determined through direct measurements, and the data are used to calculate the fuel-to-steam efficiency. Accurate results for the average operational efficiency of the boiler can be calculated using steam and fuel totalizer data.

Heat Loss or Indirect Method

Known as the indirect method, this procedure is often used when fuel usage or steam output is not available. It is calculated by subtracting the stack, blowdown, shell, and miscellaneous losses, in percent, from 100. Since miscellaneous losses are usually very small, they can often be ignored. This measurement characterizes total boiler efficiency under specific conditions and accurately reflects snapshot boiler performance only.

Stack Losses

The stack temperature is the temperature of the combustion gases (including water vapor) leaving the boiler and reflects the energy that did not transfer from the fuel to the steam or water. It is a good indicator of boiler efficiency. The lower the stack temperature, the more effective the boiler design, and the higher the fuel-to-steam efficiency. A rule-of-thumb sometimes used is that a 1% gain in boiler efficiency can be achieved with each 40°F (22°C) reduction in stack temperature.

Economizers, air preheaters, soot-blowing devices, and combustion aid chemicals can help reduce the stack temperature.

Another contributor to stack losses is the use of excess air beyond that needed for combustion. Excess air above the theoretical requirement is always used, because the driving force of the excess oxygen ensures that all of the fuel is burned rapidly and efficiently before it leaves the furnace. However, excess air takes energy from the fuel, because it has to be heated to the temperature of the other furnace gases. The heat acquired by the excess air becomes another loss (increasing unavailable energy) in the exit stack gas. Excess air requirements vary with the fuel and burner or stoker used.

Blowdown Losses

All boilers (except once-through boilers) use boiler water blowdown to control the boiler water chemistry within specified limits and minimize scale and corrosion on the waterside. Boiler blowdown is the intentional removal of boiler water, continuously, intermittently, or both.

While boiler water has not evaporated to steam, it still contains a great amount of heat energy that it obtained from the burning fuel. Depending on the boiler operating conditions, the heat loss from boiler blowdown can be significant. Decreases in boiler blowdown can be accomplished by improved pretreatment of feedwater, by operating the boiler at a higher concentration of dissolved solids, or by returning more condensate. Blowdown heat recovery equipment can be used to capture most of the blowdown heat, increasing the overall boiler efficiency.

Radiation and Convection or Shell Losses

All boilers have radiation and convection losses. The losses represent heat radiating from the boiler shell. Radiation and convection losses are essentially constant throughout the firing range of a particular boiler, but vary between different boiler types, sizes, and operating pressures.

Higher Heating Value

The higher heating value (HHV) is the energy produced by the complete combustion of one unit of fuel. By definition, this is the amount of heat released by a specified quantity of fuel [initially at 77°F (25°C)] once it has combusted and the products have returned to a temperature of 77°F (25°C). This value is typically used in the United States when calculating boiler efficiency (Table 31.3).

Lower Heating Value

The lower heating value (LHV) is the HHV of fuel minus the latent heat of vaporization of the water formed by burning the hydrogen in the fuel. This value is typically used in Europe when calculating boiler efficiency.

Fuel	Energy Content (HHV)		Fuel Density	
	Btu/lb	kJ/kg		
Natural gas	23 300	54 159	42.92 lb/1000 ft³	0.6875 kg/m³
No. 2 fuel oil	19 400	45 094	7.21 lb/gal	863.9 kg/m³
No. 6 fuel oil	18 800	43 699	7.95 lb/gal	952.6 kg/m³
Eastern coal	13 710	31 868		
Western coal	10 090	23 454		
Green wood	5250	12 203		

Table 31.3 Typical Fuel Energy Content and Density

Input–Output or Direct Method

In this method of calculating boiler efficiency, the energy obtained from the boiler in the form of steam is divided by the energy supplied to the boiler in the form of fuel. This number is multiplied by 100 to convert the result to a percentage. Equation (31.1) shows the calculation.

$$E = (100)(m_s)(h_s - h_{\mathrm{fw}})/(m_f)(\mathrm{HV}) \tag{31.1}$$

where E = boiler efficiency, %
m_s = steam mass flow, lb/h (kg/h)
h_s = steam enthalpy, Btu/lb (kJ/kg)
h_{fw} = feedwater enthalpy, Btu/lb (kJ/kg)
m_f = fuel mass flow, lb/h (kg/h)
HV = heating value of fuel, Btu/lb (kJ/kg)

Using Eq. (31.1) requires making several measurements during boiler operation. These measurements should be made during periods of steady boiler operation, in which the boiler has been producing steam at a constant rate for at least one hour. During the data-gathering period, the steam drum water level should be constant.

The feedwater enthalpy (h_{fw}) should be obtained before an economizer, because an economizer is an integral part of the boiler and recovers heat from the flue gas.

As previously stated, the absolute boiler efficiency value is not that important, because the actual efficiency is constantly changing with operating conditions. Rather, it is more important to focus on the relative change in boiler efficiency and the corresponding effect on purchased fuel consumption. While the adjustments below can be incorporated, unless they truly affect the comparison between a base case and an improvement, they can usually be ignored.

- Typically, the enthalpy in the feedwater (h_{fw}) after the deaerator but before the economizer is subtracted from the enthalpy of the steam (h_s), because the boiler does not have to add this amount of energy in the production of steam. If, however, boiler efficiency is used to calculate potential fuel savings for a proposed energy project, the makeup enthalpy value can be used in place of the feedwater enthalpy value to reflect the heat already added to the feedwater. Whichever value is used, it must be used consistently.

- Use superheated steam enthalpy when the boiler contains a superheater. Generally, the effect of attemperation water is ignored but can be included if desired and known.
- Complex utility boiler systems often include reheaters in addition to superheaters. If desired and known, the energy transferred to the reheat steam can be added to the numerator.
- Gaseous fuels are often measured and reported in volume units rather than mass units. Simply adjust Eq. (31.1) as needed to obtain the energy input as Btu/h or kJ/h in the denominator.
- HHV is generally used in the United States, while LHV is commonly used in Europe, for the heating value (HV) of the fuel. It is best to use the actual HV of the fuel being burned, and suppliers can often provide this value. If the actual value is unavailable, use the typical values in Table 31.3.

Heat Loss or Indirect Method

In this method, heat losses are estimated and reported as a percentage of total fuel input energy. The losses are then subtracted from 100% to show the resulting boiler efficiency. Equation (31.2) shows the calculation.

$$E = 100 - \text{Losses} \tag{31.2}$$

where E = boiler efficiency, %
Losses = total estimated heat losses, %

In theory, the calculated boiler efficiency should be the same regardless of which method is used. In practice, however, measurement errors, unsteady boiler operation, and the omission of some boiler heat losses cause the values to differ slightly. As previously stated, the absolute boiler efficiency value is not as important as the effect of a change in boiler efficiency on fuel consumption.

The heat losses usually included in this method are:

- Stack losses
- Blowdown losses
- Shell losses (radiation and convection)
- Miscellaneous losses

Stack Losses

By far, stack losses are the largest heat losses in a boiler. Many factors affect stack losses, but the largest contributors are boiler design (economizer, air preheater, watertube, or firetube), boiler load, waterside or fireside fouling, failed flue gas path component, and excess combustion air. Stack losses can represent 5 to 30% of the fuel energy. A rule-of-thumb sometimes used is that a 1% gain in boiler efficiency can be achieved with each 40°F (22°C) reduction in stack temperature. Another rule-of-thumb states that each 1% increase in excess oxygen results in a 0.5 to 1% loss of boiler efficiency.

Stack losses are generally estimated by measuring the flue gas exit temperature, ambient air temperature, and flue gas oxygen content. Carbon monoxide and carbon dioxide meters may also be present. Many new boilers are equipped with on-line instruments to measure these parameters continuously, and some boilers even adjust firing conditions automatically to optimize the fuel-to-air ratio. If on-line instruments are not available, portable instruments can be used for spot measurements.

The boiler manufacturer might provide tables or charts showing stack loss versus excess oxygen or air and net flue gas temperature. These tables are also available elsewhere, for example, the ASME PTC 4.1.

Blowdown Losses

Boiler water removed from the boiler to maintain the boiler water chemistry within specified guidelines contains a significant amount of heat. In the absence of blowdown heat recovery, blowdown losses typically represent the second largest energy loss from a boiler. Blowdown losses are usually less than 2% of the total fuel input and can be calculated using Eq. (31.3).

$$L_{\mathrm{bd}} = 100(m_{\mathrm{bd}})(h_{\mathrm{bd}} - h_{\mathrm{mu}})/(m_f)(\mathrm{HV}) \qquad (31.3)$$

where L_{bd} = blowdown losses, %

m_{bd} = boiler blowdown mass flow, lb/h (kg/h)

h_{bd} = boiler blowdown enthalpy, Btu/lb (kJ/kg)

h_{mu} = boiler makeup water enthalpy, Btu/lb (kJ/kg)

m_f = fuel mass flow, lb/h (kg/h)

HV = heating value of fuel, Btu/lb (kJ/kg)

The heating value (HV) of the fuel can be either the HHV or the LHV, depending on historical site preference. It is best to use the actual HV of the fuel being burned, and suppliers can often provide this value. If the actual value is unavailable, use the typical values from Table 31.3.

The two mass flow rates can be measured or calculated, and the enthalpy values obtained from saturated steam tables after measuring the temperature of the streams.

Boiler Size lb/h (kg/h)	Radiation Heat Loss (%)
200 000 (90 718)	0.5
100 000 (45 359)	0.7
50 000 (22 680)	0.9
20 000 (9072)	1.0

Source: Council of Industrial Boiler Owners, Energy Efficiency Handbook, latest edition.

Table 31.4 Radiation Heat Loss at Full Load versus Watertube Boiler Size

Shell Losses

Shell losses represent the radiation and convection losses from the boiler's external surfaces. Expected shell losses are typically less than 1% of the total fuel input for watertube boilers, and less than 0.5% of the total fuel input for firetube boilers, both operating at or close to full load. Expected losses assume there are no problems with the boiler refractory or cladding. Larger boilers lose a smaller fraction of their heat through radiation (Table 31.4).

Firetube boilers have lower shell losses than watertube boilers, because the shell on a firetube boiler contacts boiler water rather than combustion gas. Since boiler water has a lower temperature than combustion gas, the expected radiation and convection losses are lower.

For a given boiler, the gross magnitude of shell losses does not change significantly with boiler steam load. Therefore, if the loss is considered as a percentage of total fuel input energy, the loss percentage increases with decreasing boiler steam load.

Actual shell losses should be obtained from equipment manufacturers or estimated based on the protocol provided by ASME PTC 4.1. In situations where an exact value is not required, use Table 31.4 for watertube boilers and 0.5% for firetube boilers.

Miscellaneous Losses

Miscellaneous losses include:

- Unburned fuel in the boiler ash
- Effect of attemperation water

Generally, these losses represent less than 0.5% of the fuel input energy and are ignored.

Comparison of Methods

The following parameters may be difficult to measure:

- Fuel mass flow rate
- Fuel HV

- Flue gas temperature
- Flue gas oxygen content
- Steam flow rate

Water flow rates, pressures, and temperatures can usually be measured without significant difficulty. Steam flow rates can often be accurately estimated based on mass balance calculations involving measured feedwater flow and feedwater and blowdown tracer components. Determining which method to use usually depends on which parameters are easiest to obtain.

The average boiler efficiency for modern boilers is 80%. Individual values vary considerably depending on boiler type, size, operating conditions (load, excess oxygen, etc.), and fuel used. Table 31.5 shows boiler efficiency relative to boiler size and fuel type. Table 31.6 shows boiler efficiency relative to excess air. If the calculated value is significantly lower, the boiler might be operating inefficiently, and further investigation is warranted to determine the cause of the inefficient operation. Potential areas to investigate include:

- Optimize burners to minimize excess air
- Install blowdown heat recovery equipment
- Improve feedwater quality to increase boiler cycles
- Install economizer
- Install combustion air preheater
- Check boiler shell for hot spots
- Operate most efficient boilers at most efficient loading; lay-up other boilers
- Maintain clean surfaces on both waterside and fireside
- Check fireside for gas leaks or gas by-pass

For more information on boiler efficiency, including calculations and measurement methods, refer to the ASME PTC 4.1 Steam Generating Units and the U.S. DOE website.

Heat Transfer Surfaces

Boiler scale typically occurs when calcium, magnesium, iron, and silica, common to most water supplies, react with other contaminants present and exceed their solubility under boiler conditions. The scale forms a continuous layer of material on the waterside of the boiler tubes, causing poor heat transfer.

Scale creates a problem because the thermal conductivity of scale is an order of magnitude less than the corresponding value for mild steel. Even a very thin layer of scale can effectively retard heat transfer. In low-pressure boilers with low heat transfer rates, the scale impedes heat transfer, and boiler efficiency is lost. Deposits may

Fuel	Boiler Efficiency, %			
	10 000–16 000 lb/h (4536–7257 kg/h)	16 000–100 000 lb/h (7257–45 359 kg/h)	100 000–250 000 lb/h (45 359–113 398 kg/h)	250 000–500 000 lb/h (113 398–226 796 kg/h)
Gas	80	80	81	81
Oil	84	84	85	85
Coal-stoker	81	81	82	83
Coal-pulverized	83	83	86	86

Source: Department of Energy DOE/CS/40325-T1-Vol.2, Taback, H.T.; Macko, J.F; Thompson, R.E., Energy Efficiency of Industrial Steam Boilers. Final Report, July 01, 1982.

Table 31.5 “As Found” Operating Efficiency for Boilers

Excess Air, %	Natural Gas, %	No. 2 Oil, %	No. 6 Oil, %	Bituminous Coal, %
2.0	83.08	–	–	–
2.5	82.37	85.35	88.91	–
3.0	81.68	84.63	86.11	87.58
3.5	80.71	83.61	85.22	86.74
4.0	79.72	82.57	84.22	85.79
4.5	78.60	81.40	83.08	84.72
5.0	77.31	80.05	81.78	83.48
5.5	75.32	78.51	80.27	82.07
6.0	74.03	76.68	78.51	80.40
6.5	72.01	74.52	78.43	78.42

Data are representative of boilers equipped with economizers and air preheaters.
Source: Council of Industrial Boiler Owners, Energy Efficiency Handbook, latest edition.

Table 31.6 Typical Boiler Efficiencies for Common Fuels versus Excess Air

build up to a point where they completely block the boiler tube. At the higher heat transfer rates normally found in higher-pressure boilers, the scale causes the carbon steel tube temperature to increase dramatically, and the metal begins to deteriorate as temperatures exceed 900°F (482°C). Tube failure is typically noted rather than significant efficiency loss in these boilers.

Fuel waste due to boiler scale may be up to 2% for watertube boilers and up to 5% in firetube boilers. Energy losses as a function of scale thickness and composition are shown in Table 31.7.

Scale Thickness, inches (mm)	Fuel Loss, % of Total		
	Scale Type		
	Normal	High Iron	Iron Plus Silica
1/64 (0.4)	1.0	1.6	3.5
1/32 (0.8)	2.0	3.1	7.0
3/64 (1.2)	3.0	4.7	–
1/16 (1.6)	3.9	6.2	–

“Normal” scale is usually encountered in low-pressure applications. The high iron and iron plus silica composition results from high-pressure service conditions.
Source: DOE Steam Tip Sheet #10, Revised June 2001.

Table 31.7 Boiler Energy Loss Due to Scale Deposits

Multiple Boilers

A boiler generally produces its maximum efficiency at about 80 to 85% of rating or design steam capacity. Therefore, a powerhouse with a number of boilers in operation gains by judicious loading of each unit. However, a boiler with full heat recovery may have such an advantage in efficiency over one with no heat recovery that it would be better in the overall picture to run the more efficient boiler even at lower ratings than to run the less efficient at its optimum rating. During a period of increased steam demand, the most efficient generators should be loaded first. Optimizing performance requires experience and study.

Alternate Fuels

Many boilers have the ability to burn multiple fuels, such as natural gas and oil or coal and wood. Since the quality of fuel (HV, moisture, sulfur, and ash content) can greatly affect boiler efficiency, the fuel or fuel ratio used should be chosen carefully. Compliance with government regulations must also be considered. Perhaps the easiest way to establish a cost-effective fuel strategy is to compare all fuels based on operating cost per million pounds (kilograms) of steam generated. This requires that the fuel price per million Btu (kJ) be established. Special handling, storage, maintenance, transportation, and other costs (soot blowing, ash removal, and emissions control) for the use of individual fuels should be added to the fuel price if known. Lastly, since different fuels have different combustion efficiencies, the expected boiler efficiency relative to a specific fuel must be considered as well. Table 31.8 shows a hypothetical comparison of the operating cost for various fuels.

Reduce Steam Demand

A reduction in steam demand can usually be accomplished by maintaining the steam distribution system in good physical condition and by optimizing the operation of steam using process equipment.

Steam pipe leaks should usually be repaired as quickly as possible. Not only do steam pipe leaks present a physical hazard, but they also result in considerable energy waste. Tables 31.9 and 31.10 estimate steam loss per hour at various pressures using Napier's formula. Steam traps that fail open are a form of steam leak and probably account for a large portion of steam loss, relative to pipe leaks, within a facility. They are also more difficult to find. It is common to find 15 to 20% of a trap population not working properly, although not all of these will be failed open. A maintenance program

Fuel	Price/Sales Unit	Cost*/ 10^6 Btu (Cost/GJ)	Total Cost†/ 10^6 Btu (Total Cost/ GJ)	Boiler Efficiency (%)‡	Steam Cost§ ($/hour)
Natural gas	$8.00/1000 ft^3 ($0.28/m^3)	$8.00 ($7.59)	$8.00 ($7.59)	81	1000
No. 2 oil	$2.00/gal ($0.53/L)	$14.30 ($13.56)	$14.75 ($13.99)	85	1750
No. 6 oil	$1.50/gal ($0.40/L)	$10.04 ($9.52)	$11.30 ($10.72)	85	1340
Coal¶ (stoker)	$40/ton ($44.09/tonne)	$1.46 ($1.38)	$2.10 ($1.99)	82	260

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*Using values from Table 31.3.

†The total cost estimate includes costs to use fuel, which depend on equipment, equipment age, fuel impurities, soot blowing, local ash disposal, and maintenance. The projected increase based on these items may not be representative of individual circumstances. In addition, the biggest obstacle in burning No. 6 oil or coal is often the initial capital cost of equipment.

‡Using values from Table 31.5.

§100 000 lb/h (45 360 kg/h) saturated steam at 600 psig (4.1 MPag) with 1203.4 Btu/lb (2798 kJ/kg) enthalpy and 5 psig (34.5 kPag) deaerator with liquid enthalpy of 195.45 Btu/lb (454.42 kJ/kg). The deaerator liquid enthalpy is subtracted from the steam enthalpy. Steam cost shown excludes cost of water, chemicals, sewer, pretreatment, labor, etc.

¶Eastern coal from Table 31.3.

Table 31.8 Hypothetical Comparison of Cost to Burn Alternate Fuels

Gauge Pressure (psig)	Nozzle Diameter (inches)							
	1/8	1/4	3/8	7/16	1/2	3/4	7/8	1.0
	Flowrate (lb/h)							
5	12	50	112	153	200	449	611	798
10	16	63	141	192	251	564	768	1003
15	18	74	166	226	295	663	903	1179
20	22	88	199	270	353	795	1082	1413
26	26	103	232	315	412	927	1261	1647
51	41	165	372	506	661	1487	2023	2643
100	72	289	651	886	1158	2605	3545	4631
150	104	416	935	1273	1662	3740	5091	6649
200	135	542	1219	1659	2167	4876	6636	8668
250	167	668	1503	2045	2672	6011	8182	10 686
300	199	794	1787	2432	3176	7146	9727	12 705
350	230	920	2070	2818	3681	8282	11 273	14 723

Table 31.9 Steam Loss versus Nozzle Size and Pressure (U.S. Units)

Gauge Pressure (kPag)	Nozzle Diameter (mm)							
	3.2	6.4	9.5	11.1	12.7	19.1	22.2	25.4
	Flowrate (kg/h)							
35	6	22	51	69	90	202	276	360
70	7	28	64	87	113	255	347	453
100	8	33	75	102	133	300	408	533
140	10	40	90	122	160	360	489	639
180	12	47	105	143	186	419	571	746
350	19	75	168	229	299	674	917	1198
689	33	131	295	402	525	1181	1607	2100
1034	47	188	424	577	754	1696	2309	3016
1378	61	246	553	753	983	2212	3011	3932
1723	76	303	682	928	1212	2727	3712	4849
2067	90	360	811	1103	1441	3243	4414	5765
2412	104	418	940	1279	1670	3758	5115	6681

Table 31.10 Steam Loss versus Nozzle Size and Pressure (Metric Units)

focused on finding and repairing steam leaks is essential to the efficiency of a steam system.

Insulation is another aspect to monitor closely. Insulation can typically reduce energy losses by 90%. Insulation assures that steam quality and pressure are maintained from the boilers to the point of use. Damaged, inadequate, or missing insulation allows steam to condense early, giving up a portion of its heat as radiation and convection losses. This loss can be significant. For example, at 100 psig (689 kPag) steam contains 1190 Btu/lb (2766 kJ/kg), whereas condensate contains only 309 Btu/lb (719 kJ/kg). Insulation should be quickly repaired or replaced following any maintenance work. Valves and flanges are often left uninsulated and can result in significant energy loss.

Unused steam lines and traps should be turned off, since they can result in significant steam consumption without providing any value. Steam present in unused lines condenses; it might be recovered, or it might be discarded. The steam does not provide useful work and may even result in corrosive damage to the system. Unless isolated, the pipe remains at pressure with a continuous supply of steam to condense.

Proper steam system design improves operational efficiency. Poorly designed systems are most likely to function improperly and fail early. Steam systems should be designed with adequate metering to be able to track steam consumption and routinely monitor usage on a facility-wide basis. Ideally, high-pressure steam should not be reduced through pressure control valves. Venting of steam at any pressure should be minimized, unless it is necessary for the proper operation of specific equipment, such as a deaerator.

Reduce Boiler Blowdown

Boiler blowdown contains a tremendous amount of heat, and efforts to reduce the quantity of blowdown can save both energy and money, if blowdown heat recovery is not utilized. The blowdown rate from a boiler should be established based on several parameters:

- Boiler pressure
- Feedwater silica, conductivity, and alkalinity
- Steam purity required
- Potential for contamination of the feedwater or condensate

The simplest approach to reduce boiler blowdown is to increase the cycles of concentration (COC). However, this must be accomplished carefully and thoughtfully to avoid creating operating problems, such as boiler water carryover into the steam and boiler deposits. The "Consensus on Operating Practices for the Control of Feedwater and Boiler Water Chemistry in Modern Industrial Boilers" (CRTD, Volume 34, latest revision) published by ASME is a good guide to determine the maximum COC for a boiler. If exceeding the ASME guidelines is desired, boiler testing, such as steam purity studies to determine carryover and transport studies to determine deposition, should be conducted. Typically, adhering to the ASME guidelines provides reliable results.

In systems using only manual control of boiler blowdown, installation of automatic blowdown control can often be justified. Because automatic blowdown controls can limit the boiler water conductivity to within 5% of the set point, the average facility might reduce boiler blowdown by about 10 to 20%, when changing from manual control.

The internal treatment program can affect maximum COC. Inorganic additives, such as sulfite and phosphate, contribute to boiler water conductivity, which is one of the ASME limits. In some cases, changing to organic treatment products can reduce boiler water conductivity and allow higher COC. This approach should be evaluated on a case-by-case basis.

If further increase in COC is desired, improved makeup water pretreatment can be considered. For example, replacing conventional ion exchange softeners with demineralizers or reverse osmosis (RO) membranes, allows higher COC by reducing the mineral content of the makeup water. This is akin to higher condensate recovery discussed below. However, the upgraded makeup water pretreatment is more expensive, in both capital and operating costs. For each application, the increased makeup water pretreatment costs must be compared with the decreased boiler operating costs, to determine if this project is justified.

Savings that can be achieved by higher COC are significantly lower, if blowdown heat recovery exists.

Recover Blowdown Heat

During the boiler blowdown process, water is discharged from the boiler to mitigate scale formation, corrosion, and boiler water carryover. However, boiler blowdown wastes energy, since the lost liquid is at about the same temperature as the steam. Much of this heat can be recovered by routing the boiler blowdown through a flash tank to recover low-pressure steam and to a heat exchanger that preheats the boiler makeup water.

Typical blowdown flows range from 0.5 to 20% of feedwater flow. Any boiler with continuous surface blowdown exceeding 1% of the feedwater flow rate is a good candidate for blowdown heat recovery. The heat exchanger should be located downstream from the makeup water pretreatment process to minimize fouling of the heat exchanger.

The heat recovery potential depends on boiler size, system pressure, annual hours of operation, boiler load, and the boiler COC. Heat recovery potential can be calculated using Eq. (31.4):

$$\mathrm{HR} = (m_{\mathrm{bd}})(h_{\mathrm{bd}} - h_{\mathrm{mu}})E \tag{31.4}$$

where HR = heat recoverable, Btu/h (kJ/h)

m_{bd} = blowdown mass flow, lb/h (kg/h)

h_{bd} = blowdown enthalpy, Btu/lb (kJ/kg)

h_{mu} = makeup enthalpy, Btu/lb (kJ/kg)

E = heat recovery equipment efficiency, decimal

An important advantage of continuous blowdown is that it permits heat recovery from the blowdown water. The use of a blowdown flash tank and heat exchanger minimizes the heat losses and maximizes energy reuse. Flash tanks permit the recovery of low-pressure steam that may be used in the deaerator or air preheat coils; the use of a heat exchanger allows for the recovery of additional heat from the hot flash tank water. In a low-pressure system, a heat exchanger can be used by itself.

Flash tanks are of benefit only when additional low-pressure steam can be used (e.g., in a deaerator, air preheat coils, and process heater). Blowdown heat exchangers are most often used to preheat boiler makeup water before the deaerator, but can be economically used to heat process streams. Figure 31.3 shows a typical heat recovery system.

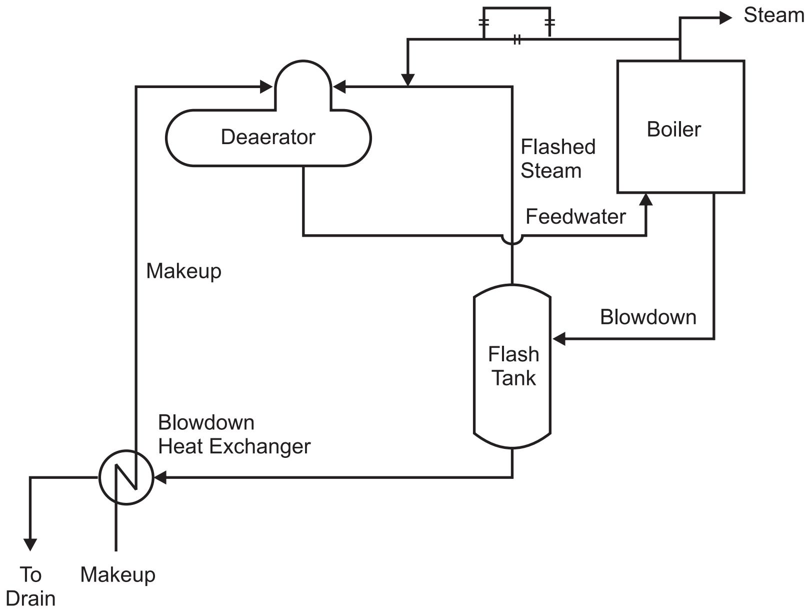

Figure 31.3 Typical boiler blowdown heat recovery system.

The blowdown heat exchanger must be installed in a location where inspection, maintenance, and cleaning can occur, at least during boiler outages. Installing the exchanger in a remote, nonaccessible location only means loss of heat transfer efficiency over time and energy (money) lost. Installation of simple dial temperature gauges on the inlet and outlet of the makeup water and blowdown is highly recommended. Although mass flows are not exact, a reasonable energy balance can be done with this simple, inexpensive equipment (making sure they are visible to workers). By using simple temperature monitoring, the decision on whether to schedule cleaning or maintenance of the blowdown heat exchanger can be made.

Flash Tank

Flash tanks are commonly used to generate flash steam, supplementing steam generated in fired boilers. Flash steam is often used in the deaerator. The flash steam is generated by directing continuous boiler blowdown, condensate, or other hot water stream to a flash tank that operates at a lower pressure. The lower pressure environment allows some of the water to flash, creating the flash steam, while most of the water remains liquid at lower pressure and temperature. The most common use of a flash tank is to recover heat from boiler blowdown.

In some lower-pressure systems, a flash tank is used only to reduce the pressure and temperature of water before discharge.

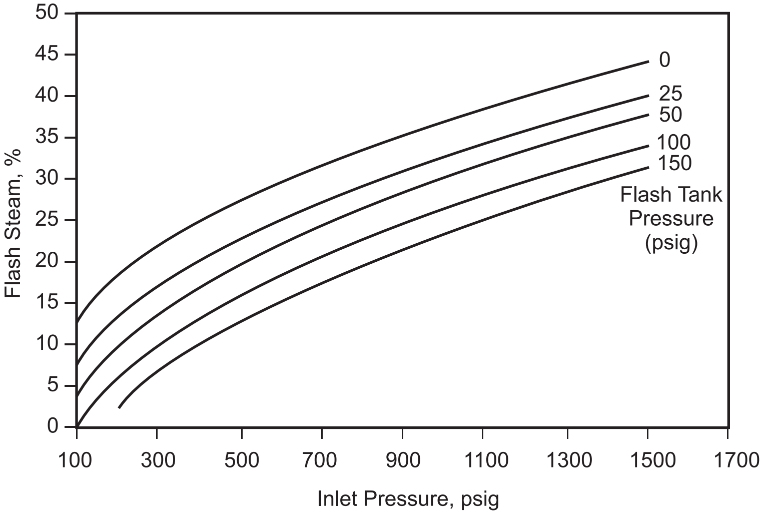

FIGURE 31.4 Percent flashed steam from flash tank.

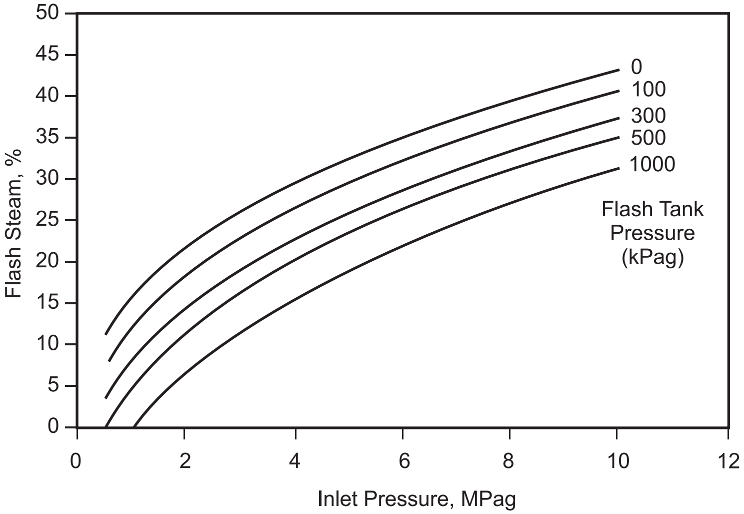

FIGURE 31.5 Percent flashed steam from flash tank (metric units).

In these systems, the flash tank is not used to recover heat and generally operates at atmospheric pressure.

Figures 31.4 and 31.5 shows the amount of flash steam available at various inlet and flash tank pressures. The amount of flash steam from a flash tank can be calculated using Eq. (31.5):

$$m_{\mathrm{fs}} = (m_i)(h_i - h_{\mathrm{fl}})/(h_{\mathrm{fs}} - h_{\mathrm{fl}}) \tag{31.5}$$

where m_{fs} = flash steam mass flow, lb/h (kg/h)
m_i = inlet mass flow, lb/h (kg/h)
h_i = inlet liquid enthalpy, Btu/lb (kJ/kg)
h_{fl} = flash tank liquid enthalpy, Btu/lb (kJ/kg)
h_{fs} = flash tank steam enthalpy, Btu/lb (kJ/kg)

The flash tank recovers energy in the form of steam that otherwise would be lost, and reduces the required boiler steaming rate. The recovery of heat using flash steam from boiler blowdown typically recovers 30 to 80% of the heat that is otherwise lost.

Optimize Condensate Recovery

Returned condensate, being condensed steam, is of high purity and has a relatively high heat content, making it ideal, both economically and technically, for boiler feedwater. Economically, the more condensate returned, the less makeup water required, thereby saving on both water and feedwater pretreatment costs. The high purity of condensate allows the boiler to operate at higher COC while maintaining conductivity standards, thereby reducing costly water and energy losses to boiler blowdown. The higher heat content of condensate [158 Btu/lb at 190°F (367 kJ/kg at 88°C)] as compared to makeup water [28 Btu/lb at 60°F (65 kJ/kg at 15.6°C)] directly reduces the fuel requirements of the boiler to convert feedwater into steam. All condensate collection tanks and return lines should be insulated to assure that condensate is returned at the highest temperature possible.

Technically, the high purity of condensate reduces the overall scale-forming tendency of boiler feedwater, regardless of the sophistication of the makeup water pretreatment system. This results in cleaner heat transfer surfaces and optimal heat transfer rates. Higher quality feedwater reduces the possibility of boiler tube failure due to excessive scaling.

To realize the benefits of a condensate return system, a program of corrosion control must be implemented. Left untreated or treated improperly, condensate can become very corrosive to plant piping and equipment. The resulting products of corrosion can enter the feedwater and form harmful, tenacious deposits on boiler heat transfer surfaces. The lack of condensate corrosion control can ultimately result in the loss of heat transfer efficiency and ruptured boiler tubes, a leading cause of unscheduled plant shutdowns.

Reduce System Pressure

Oversized boiler plants with steam distribution systems using saturated steam are potential candidates for reducing the steam system operating pressure. Steam pressure reduction is accomplished by lowering the boiler pressure. This action typically affects only the highest-pressure part of the steam system. Pressure reducing valves provide the correct pressure in the lower pressure portions of the system—at least in theory.

Savings are primarily in the high-pressure section of the system. They result from reduced energy losses in multiple areas such as steam leaks, boiler radiation and convection loss, piping heat loss, steam trap leakage, combustion loss, and blowdown heat loss. In addition, since the boiler is operating at a lower pressure, less fuel is required to boil a pound (kilogram) of water.

While energy savings can certainly result from reducing steam pressure, there are a significant number of problems that can occur and that may reduce the operational effectiveness of the system. Pressure reducing valves, safety valves, flow devices, and high-pressure steam traps may not work properly and may need to be replaced. Boiler carryover may readily occurs causing wet steam, steam system erosion, and water hammer. Circulation problems may occur in watertube boilers, leading to tube blockage and overheating. Lower steam pressure increases steam velocity within a pipe, and this may lead to excessive noise and pressure drop.

Pressure reduction is not to be taken lightly. A full assessment of the boiler plant and steam system should be made before any attempt at pressure reduction. This assessment should include analysis of the average and peak steam loads in relation to plant capacity. Data on piping, insulation, pressure reducing valves, safety valves, and steam trap condition should be collected. Lastly, steam pressure reduction should be tested to establish the minimum workable pressure for a steam load that is above average but below peak. This test will improve reliability of savings estimates.

Anyone considering steam system pressure reduction for energy savings is encouraged to read the U.S. DOE Steam Technical Brief, "Steam Pressure Reduction: Opportunities and Issues," DOE/GO-102005-2193.

Optimize Turbine Operation

Power plants that operate condensing turbines can justify careful attention to maintaining a clean condenser. Good heat transfer here means better vacuum and more heat energy available to the turbine. As a rule-of-thumb, unit efficiency decreases by 1 to 2% per inch Hg decrease in backpressure (0.3–0.6% per kPa). Power plants with condensing turbines are not very efficient, as they tend to use only 30 to 43% of the available steam thermal energy, with the remainder lost to the environment when steam is condensed in the condenser.

Most industrial turbines are backpressure or extraction turbines. A condensing turbine may also be present at the facility but is typically used only to balance the steam and electrical demands. A system with both types of turbines is most efficient, when operated at maximum extraction and minimum condensing. An industrial plant burning oil, finds it cheaper in most cases, to buy power than to try to produce it by operating a turbine, where the steam must go to a condenser. However, power generated with extraction or in noncondensing turbines usually costs less than purchased power. This is the essence of the trend toward cogeneration, or "topping" a process need for steam with a turbine exhausting to the process steam line.

Figure 31.6 shows the operating constraints on an extraction turbine generating electric power and exhausting the used steam to a process. The process requirements have a direct bearing on how

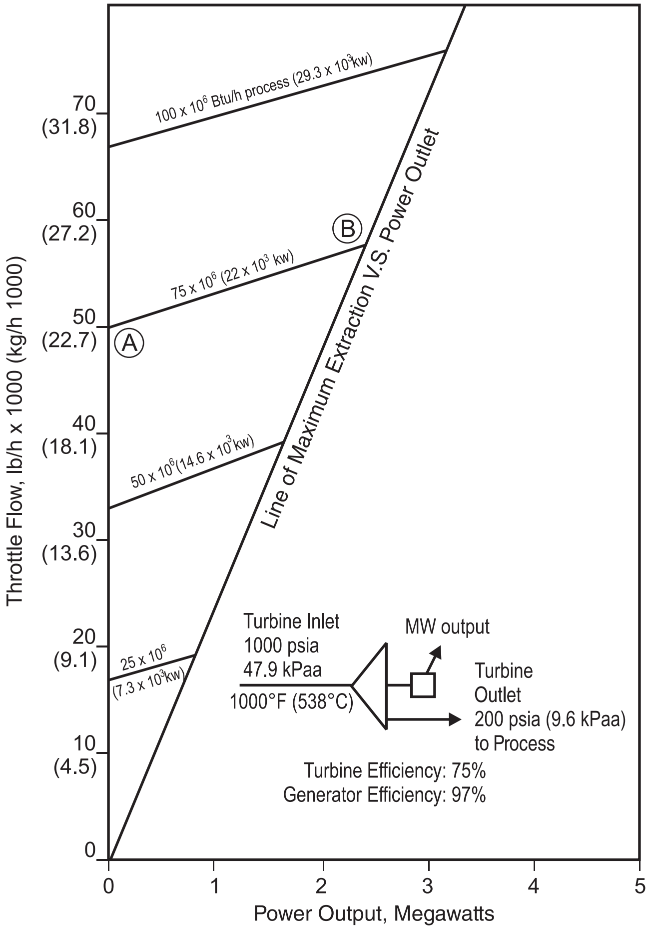

Figure 31.6 Throttle flow versus power output at various process steam requirements for fictional noncondensing turbine. Point A represents no electric load; point B represents maximum load.

much power can be generated. Generally, process requirements are rated in Btu/h (kJ/h) and easily converted to pounds per hour (kilograms per hour) based on the enthalpy of the steam.

If the process requires 75 million Btu/h (79 million kJ/h), which is 50 000 lb/h (22 680 kg/h), the power plant could theoretically generate zero power (Fig. 31.6 point A) or progressively up to approximately 2.4 MW (Fig. 31.6 point B), while at the same time supplying the required energy to process. However, in going from zero to 2.4 MW, the turbine throttle flow increases from 50 000 to 57 000 lb/h (22 680–25 850 kg/h). Even though the steam flow increased, the Btu (kJ) per hour to the process remains constant, because the enthalpy in the exhaust steam decreases a proportionate amount.

Some industrial systems are operated to supply a constant electrical demand. As steam demand fluctuates, excess steam not needed by the process may be vented. These systems should consider using a portion of the vented steam to increase feedwater or process water temperatures. Each 10°F (5.6°C) increase in feedwater temperature usually results in a 1% savings in total fuel input, for a typical industrial steam plant that has excess exhaust steam. There is a maximum feedwater temperature, however, which is determined by equipment design. A feedwater temperature that is too high can cause economizer and boiler circulation problems.

SECTION 5

Industries

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CHAPTER 32

The Paper Industry

We interact with paper-related products countless times during our daily activities and these interactions can be very different. On one hand, we might bring a new appliance into our house in a cardboard box, where linerboard grade paper laid over corrugated medium provides protection for the product. On the other end of the spectrum, tissue and towel grades of paper touch us in more delicate ways than the corrugated medium. It would be accurate to say there is no single paper industry; rather, it is a collection of industries that produce different grades of paper to serve us in many different ways.

As a major user of water, the paper industry is challenged to balance its water use to meet economic, social, safety, and environmental objectives. Water is one of the major lifelines in the paper making process. It is used as a medium to transport pulp, conduct and retain heat, form a finished product and remove contaminants. Without it, different grades of paper cannot be made. On average, 7800 gallons of water are required to produce one ton of paper product (FisherSolve database). According to the National Council for Air and Stream Improvement (NCASI), water is typically recirculated within the paper making process up to 10 times in the mill before discharge and 88% of the influent water is returned back to waterways. The remaining water is lost through evaporation, within the final product or included in sludge waste. Figure 32.1 shows the typical water footprint of an integrated mill.

When leaving the headbox of a paper machine, the stock solution is typically 99% water and 1% fiber, as shown in Fig. 32.2. In tissue manufacturing, the consistency might be as low as 0.2% fiber, with 99.8% of the mass being water. When the production process is completed and the sheet is taken up on a reel, the final product may be about 5% water and 95% fiber. Therefore, the paper machine, the essential production component in the papermaking process can be seen as doing two primary tasks. First, it organizes the fibers and

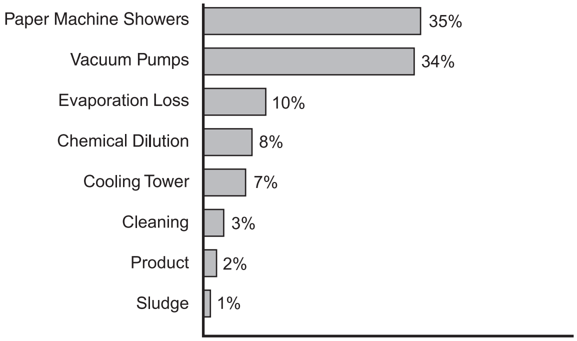


Figure 32.1 The typical water footprint of a nonintegrated mill. (*Source: Data compiled from Nalco Water sources*.)

additives intended to give the final sheet its desired properties, in accordance with the specifications of that grade of paper. Secondly, it extracts water from the sheet as economically as possible. That is papermaking in its most simple terms, and managing water quality and demand is an integral component of the task.

With growing concerns of water scarcity, the paper industry is striving to reduce overall water demand to achieve a more sustainable approach to pulp and paper manufacturing. For example, in Fig. 32.3, the U.S. pulp and paper industry significantly reduced its water usage over the last 30 years. The rate of decline of water use has slowed in recent years mainly due to economic barriers to reuse and recycle water while maintaining productivity and meeting product quality specification. As a mill becomes more water closed, the water environment evolves into a new state that most likely introduces and

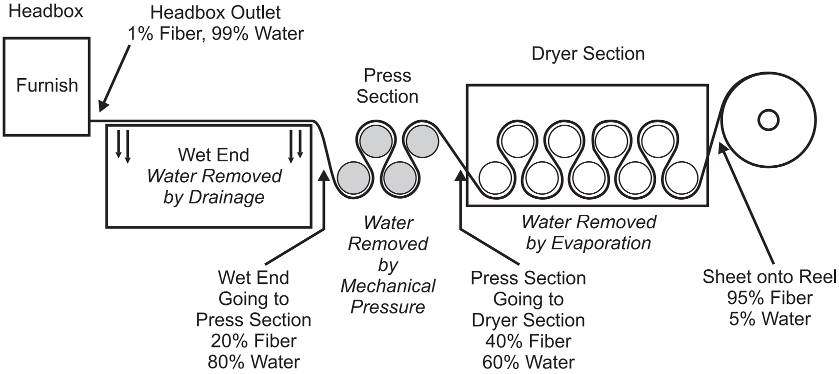


Figure 32.2 Water and fiber mass fractions along a paper machine.

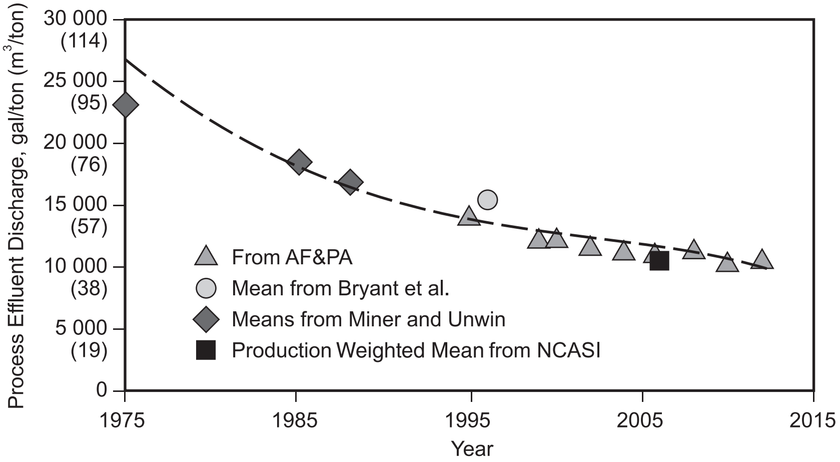


FIGURE 32.3 Trend of effluent volume in the U.S. pulp and paper industry. Note, AF&PA stands for American Forest and Paper Association. (*Source: Reuse of Process Effluents: Research Roadmap; Agenda 2020 Technology Alliance, March 2016*.)

accumulates contaminants such as suspended solids, total dissolved solids, and organic species within the system. In addition, the changing environment can have an impact on physical and chemical characteristics such as increased soluble charge, conductivity, temperature, and lower dissolved oxygen concentration. Evolving conditions can result in deposits, scale, corrosion, increased microbial activity and reduced performance of chemical programs. As these challenges unveil, high capital investments along with associated energy demands, maintenance and real estate footprint would need to be considered as part of the solution. These investments along with the low cost of water often become the main hurdle to execute water closure projects.

The importance of economical paper production cannot be overstated. Paper producers are not only competing with each other for market space, but they must also compete with other products or media that can provide the same functions as those made of paper. In the grocery store checkout line, we might be asked “paper or plastic?” This is a case where a paper-derived product is directly competing with one made from petroleum. In other examples the competition might not be seen as so direct. For example, the Internet supersedes the daily newspaper as the primary source for current information about the world around us.

This competition demands that paper producers be incredibly focused and agile on providing the precise performance characteristics when marketing their products. Whether it is strength in packaging materials, softness in tissue grades, or printability in graphic and specialty grades, producers try to make paper in a cost-efficient manner with minimum downtime of fixed-cost assets and use of natural resources. Industry operating teams know whether their paper machine is operating on a world-class basis, making them a so-called reference machine that all others strive to match, or if they fall into the dreaded fourth quartile, where any change in product demand or cost structure may target that mill or machine for closure. The one sure thing about the paper industry is the constancy of change. These changes include an influx of new competition from other sources that take market space from paper, such as cost of raw materials and energy required for production, regulatory concerns and general changes in the global market where supply and demand move constantly.

There are other products that are sometimes associated with paper production that are important in their own ways, but secondary in terms of volume and value. Wood is still a valued construction material, and there are still saw mills that cut trees into lumber. In addition, lumber is not always the form that a wood-derived construction material will be made. Plywood, chipboard, and Oriented Strand Board (OSB) are widely used in building construction. In addition, organic chemicals found in wood in widely differing amounts can be extracted for any number of industrial purposes. Turpentine is derived from what we might call the sap of pine trees, and it is still used in paint and coating applications. Tall oil can be similarly extracted from wood during the production process, and it is used in a number of industrial chemicals. Novel uses for waste materials from the papermaking process are put into practice continuously. Recycled fibers that are not acceptable for paper production, are mixed with grass seed in such a way that the fiber holds moisture to improve seed germination as it is applied to poor soils or areas subject to erosion before the grass roots can take hold. Waste wood or fiber that cannot be otherwise used for paper production has a considerable value as an energy source. In most cases, the paper mill uses the fuel value of these wastes to generate the steam and electricity needed to produce the paper. In some cases, there are stand-alone power stations that burn wood waste and supply electricity to the distribution grid.

Industry Profile

Table 32.1 shows paper production rates on a global basis in 2016. The global perspective is particularly important to consider, because both supply needs and demand capabilities are changing rapidly.

The North American and Western European Paper consumer markets are considered mature with minimal or no growth in the volume of paper-related products sold. However, consumer markets in Eastern Europe, Greater China, and Asia Pacific are growing.

Major Grade	% of Global Production Asia Pacific (excludes Greater China)	Europe	Greater China	Latin America	North America
Market Pulp	11%	14%	7%	50%	18%
Newsprint	9%	7%	2%	1%	5%
Packaging	46%	43%	66%	31%	48%
Printing and Writing	25%	23%	14%	8%	16%
Specialties	4%	6%	4%	1%	4%
Tissue and Towel	6%	8%	8%	9%	9%

Source: Compiled using data from FisherSolve.

Table 32.1 Global Paper Production Statistics, by Grade

These areas are increasing their production capabilities, and they may not be export targets for producers in the more mature geographic areas. Latin America exhibits growth in paper product consumption, but it is a rapidly growing producer of market pulp, in addition to finished paper products.

Along with segmentation by paper grade produced, the paper industry is segmented by fiber source used in the process and might be called feedstock. In most cases, the highest value paper products are associated with those mills using virgin fiber, in other words, trees as the starting point for their production processes. Converting a tree into a finished sheet of paper or bale of pulp requires a considerable number of unit operations, and therefore is considerably capital intensive. The availability of water is equally important. Most mills in the world are in areas with both extensive forests and access to large volumes of water. The southeastern United States, Scandinavian region, Brazil in Latin America, and Indonesia in Asia meet these requirements, and are recognized areas where virgin fiber pulp and paper mills are located.

However, there are disparities in these regions as to the intensity of tree farming, which is becoming a primary source of fiber supply to the mill. In an area such as northern Canada, the growing season for a tree is quite short, and mills require trees to have a longer grow period, perhaps 25 to 35 years. Therefore, trees are sent to the mill from further distances. A contrast to this would be Brazil, where selective breeding of Eucalyptus tree has resulted in tree farms that can be harvested in amazingly short time periods. Trees 7 to 10 years old are commercially usable in this region, and further improvements in the growing processes are still being pursued.

As previously stated, paper production often requires large volumes of water for various unit operations. Table 32.2 shows typical water use per ton (tonne) of production by paper grade produced, and its relativity to world areas where production occurs.

These values follow trends that might be expected based on a cursory understanding of the processes used. Tissue production typically uses market pulp supplemented with recycled fiber as a feedstock, and the pulping processes to convert a tree into usable fiber are not often present. Therefore, water usage associated with these pulping, and especially bleaching operations, is not present. Behind packaging, tissue production requires the second least water per ton (tonne) of production. Newsprint is increasingly made from recycled fiber sources, which requires less water than other production methods.

Market pulp, specialties and printing grades require the most water. These grades are being made to higher brightness or whiteness standards, and contaminant removal to achieve these specifications demands more production process steps as well as water usage. The packaging grade of paper shows the widest range of water utilization. In cases where virgin fiber is used, water use can be high. Some packaging grade mills using recycled fiber as feedstock operate with a zero-liquid discharge (ZLD) where no wastewater is discharged. In these mills, water discharges to the atmosphere through process evaporation and drying of the sheet in the dryer section; in addition, through sludge waste and in the final paper product. Not surprisingly, water reuse and recycle procedures in these mills are most advanced, and the volume of influent is low.

Virgin Fiber Production

Despite ever-increasing efforts to maximize recycling of existing paper products; there still is a considerable need to harvest trees for paper production. With well-managed tree farms now the norm, wood is seen more as a crop than an irreplaceable resource. While requiring more processing steps than recycled fiber supplies, virgin fiber is preferred for the production of several important paper grades.

Wood Yard Operations

A tree destined to become paper, enters the mill through the wood yard. Some mills receive whole trees (called "longwood") on trucks or rail cars. Logs can also come into the wood yard precut to a specified length. Wood in this form is called bolts. Trucks or rail cars are also used to deliver trees in this form. Some mills receive wood already chipped to the specification of their process, and other than

Major Grade	Water Usage ('000's)					
	Asia Pacific—All Other USG/ton (m^3/tonne)	**Europe USG/ton (m^3/tonne)**	**Greater China USG/ton (m^3/tonne)**	**Latin America USG/ton (m^3/tonne)**	**North America USG/ton (m^3/tonne)**	**Grand Total USG/ton (m^3/tonne)**
Market Pulp	12.1 (0.05)	9.42 (0.04)	8.22 (0.03)	9.27 (0.04)	18.4 (0.08)	57.4 (0.24)
Newsprint	13.9 (0.06)	4.76 (0.02)	4.88 (0.02)	6.89 (0.03)	12.3 (0.05)	42.7 (0.18)
Packaging	12.1 (0.05)	4.52 (0.02)	3.64 (0.02)	5.03 (0.02)	6.65 (0.03)	31.9 (0.13)
Printing and Writing	15.7 (0.07)	5.39 (0.02)	4.30 (0.02)	8.00 (0.03)	17.7 (0.07)	51.2 (0.21)
Specialties	14.1 (0.06)	8.55 (0.04)	4.46 (0.02)	10.2 (0.04)	18.3 (0.08)	55.6 (0.23)
Tissue and Towel	10.3 (0.04)	3.83 (0.02)	3.20 (0.01)	6.97 (0.03)	12.2 (0.05)	36.5 (0.15)
Grand Total	78.1 (0.33)	36.4 (0.15)	28.7 (0.12)	46.3 (0.19)	85.63 (0.36)	275.3 (1.15)

Source: Compiled using data from FisherSolve.

TABLE 32.2 Water Usage per Ton (Tonne) of Paper Production, by Grade and Region chip storage, have minimal wood yard operations. Very few mills still have logs floating into the mill on the local surface water source anymore. This scenario is more from the industry's past than future.

Mills receiving either longwood or bolts must debark the wood before chipping. Debarking involves a rotating drum, where the bolts rub against each other and the surface of the drum. The intent is to remove only the bark and a minimal amount of useful fiber. Water is used in relatively small volumes in the debarking process. To some degree, water serves as a sort of lubricant in assisting bark removal, but more importantly, water added in the debarking process aids in minimizing dust and fiber fines generation. Wastewater from the process is laden with suspended solids and organics from the wood, and goes directly to the waste treatment primary clarifier. Water from this part of the mill is not a good candidate for reuse or recycling. Figure 32.4 is a picture of a debarking process in operation at a mill site.

Chipping

The preparation of wood chips is a seemingly simple operation, but one that has considerable importance in the process. Mechanical paper grades are made directly from wood processed through a large machine called a refiner. This is advantageous because each unit of wood mass entering this process yields about 0.9 lb (0.4 kg) of resulting pulp, the highest fractional recovery of any preparation process. (Refining is a term also used in stock preparation operations. This term has multiple uses, which can be confusing.) However, the strongest paper grades are made from a process whereby the fiber is separated from the other constituents of the wood, following a process of digestion. Preparing chips to consistent dimensions is critically important to the digestion process, since the chemicals and heat used must penetrate the chips to liberate the fiber, without degrading the fiber. Having uniforms chips is an important parameter in modern papermaking.

Figure 32.4 Bark removal from cut wood in a rotating debarking drum.

Following the chipping process, the wood is moved via conveyor to a chip storage area. In an attempt to collect stray metal that may be present, most mills today have magnets hung over various locations along the chip conveyor system. Metal would damage or otherwise interfere with downstream processing steps. Chip storage is an often-overlooked operation. A large pile of chips will quickly begin to decompose, or compost, with a resulting loss of fiber mass and quality. Some mills cannot receive wood throughout the year due to local weather conditions, and these mills typically have larger chip inventories. These mills will have bulldozers working the chip pile to prevent the composting reaction.

Very little if any water is involved in the chipping process. In a few cases, control of fugitive dust emissions from the chipping process necessitate that something be sprayed onto the chip pile. Since water would accelerate the composting reactions that decompose the wood, foam generated from water, a surfactant chemical, and air, is used so that less water mass is applied to the chips. Ideally, the foam dries into a crust on the top layer of chips, which limits the ability of prevailing winds to blow fiber fines and dust around the surrounding environment.

Groundwood Pulping

Many pieces of print advertising material need to be produced as cheaply as possible, and there is no intention that this information will need to be saved or archived. Therefore, the most economical process that can be used to make a reasonably good sheet of paper with acceptable printing characteristics is used. The pulp that becomes this sort of paper is made by simply grinding the debarked wood into individual fiber strands by pressing the wood against a rotating wheel. There is a slight loss of organic material from the wood, but nearly 90% of the wood mass entering the grinding process leaves as finished pulp when it is prepared in this way (Fig. 32.5).

Mechanical pulp is quite weak. To achieve the resulting sheet quality required, it is sometimes blended with pulp made in other ways. The primary utility used in the production of mechanical pulp is the electricity needed to rotate the grinding wheel. Producers of this pulp grade pay extraordinary attention to minute-by-minute changes in electrical costs, and can choose to stop production if the cost is too high. Water is only used to sluice the fibers from the grinding process toward final sheet production, and although a large volume of water is used in this process, its quality is not so important. Water reuse is not widely used, because of the tendency of the water to extract organics from the pulp. Too high an organic content can make production of acceptable sheet brightness difficult to achieve.

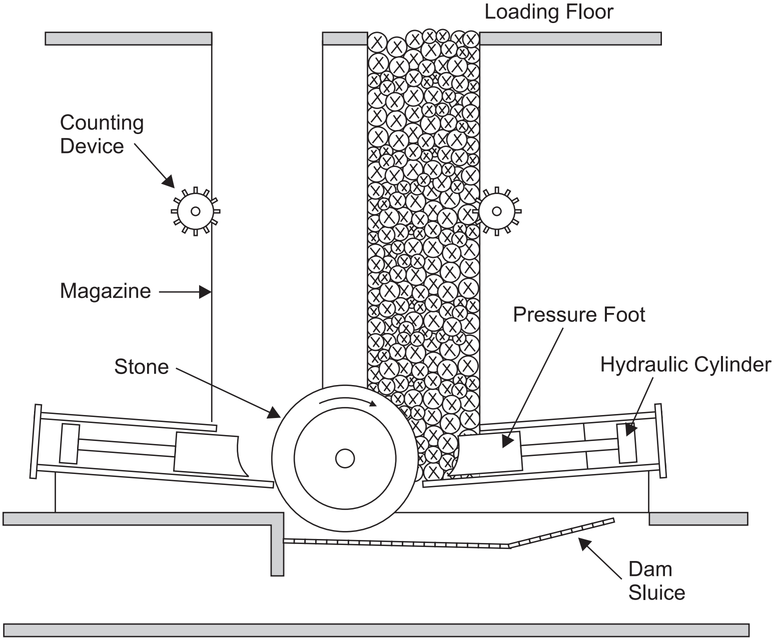


FIGURE 32.5 Logs are forced against a grinding stone to produce groundwood pulp. (*Adapted from Pulp and Paper Science and Technology, Volume 1: Pulp, McGraw-Hill, 1962.*)

Thermomechanical Pulping

An advancement over groundwood pulping for the production of primarily newsprint grade paper that has come into widespread use in the industry is thermomechanical pulping, often simply called TMP. The application of steam to the wood chips in a confined chamber allows for pulp of better quality, resulting in better sheet strength. TMP rivals chemical pulp in quality, but uses considerably less water, chemicals, and energy. While the fiber yield is not as high as is achieved with mechanical pulping, it is considerably higher than what can be accomplished with a chemical pulping process. In the highly cost competitive world of newsprint paper production, the TMP process, or some derivation, has assumed the leadership position.

The TMP process begins with wood chips first washed with water. The water quality is not important at this stage, and a recycled stream is often used. Chemicals may be applied at this early stage, to have a maximum effect at partially dissolving the bonds holding the fibers together. This step is called impregnation. In some cases, this system is called CTMP, reflecting the addition of chemical to the classic TMP process. The material then passes into a heating chamber, where the direct application of steam heats and softens the fibers.

Finally, mechanical grinding results in the pulp quality required for production, with multiple adjustments being possible to yield optimal fiber length and strength.

Another version of the process is called BCTMP, where bleaching additives result in a whiter pulp for higher value paper production. Hydrosulfite and hydrogen peroxide addition accomplish the brightening of the pulp.

Chemical Pulping—Kraft Process

The last part of the 20th century saw the Kraft process become the dominant method for chemical pulp preparation in papermaking. Because of intensive recycling of chemicals, the generation of steam as a by-product, and dramatically reduced environmental impacts, the favorable performance characteristics of Kraft pulping are seen worldwide. Figure 32.6 shows the Kraft pulping process in a schematic form, and the following discussion will describe the various unit operations and the role water and steam have in many of them.

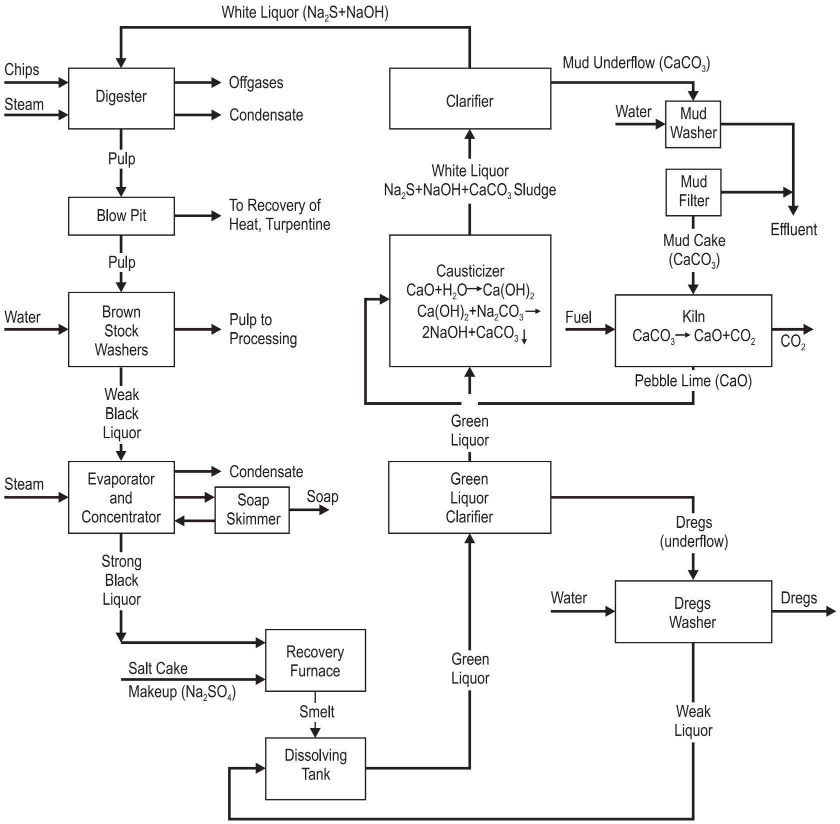


Figure 32.6 Kraft pulping process flow diagram.

Digestion

As with any cyclic process, it is sometimes difficult to find a point of entry. This discussion will start at the point where the wood chips enter. The chemicals used to dissolve the internal bonds holding the wood chip together are sodium sulfide and sodium hydroxide. These chemicals called white liquor when combined together, contact the chips in a pressurized vessel called the digester. In earlier times, batch digesters were the norm, and a mill would have a series of these vessels in a line to provide a nearly continuous supply of pulp. Continuous digesters are now the norm, and the Kamyr brand (Fig. 32.7) is nearly ubiquitous. After a contact period of about an hour at a temperature near 250°F (121°C), depending on the species of wood, complete chip heating and dissolution of the bonding elements is achieved.

A major difference between how batch and continuous digesters function is seen in how steam is used to heat the solution. In a batch digester, steam is directly applied to the chips and chemicals. This results in no condensate being returned to the powerhouse for reuse as boiler feedwater. The continuous digester has indirect heaters,

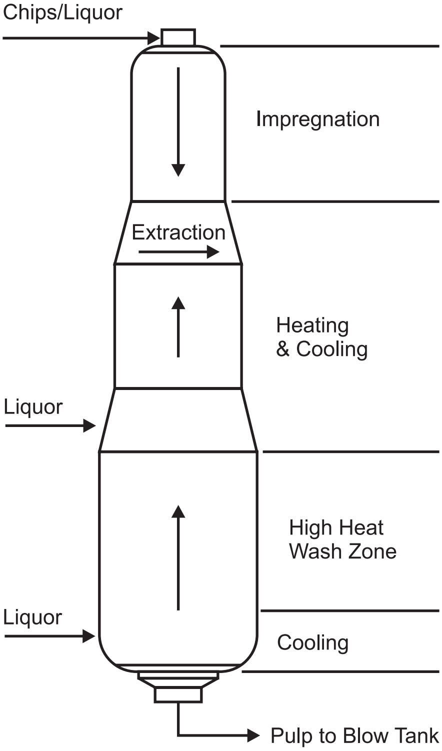


FIGURE 32.7 Compartments of continuous digester.

which adds the heat to the chemical solution across a heat exchanger. This allows the steam condensate to be returned to the powerhouse, resulting in water and energy savings. However, the possibility of chemical contamination should a heat exchanger leak, requires additional monitoring of the condensate quality, and best practice is to have diversion capability should a leak occur.

Blow Tank

The pulp leaves the digester and enters the blow tank. In the blow tank, the pressure established in the digester is released. The drop in pressure causes moisture that has penetrated the chip interior to flash, which blows the chip apart, releasing the fibers for processing as pulp. Steam vapor is condensed and collected, with process water being heated on the other side of the heat exchanger. Free water drained from the pulp and the condensate stream is routed to an evaporator system, so that the spent chemicals from the process can be collected, regenerated, and reused. Failure to collect the cooking chemicals and the waste gases associated with the process would make Kraft pulping economically unattractive and an environmental nightmare.

Brown Stock Washing

The next step in the process is called brown stock washing. Here, the pulp and water collected from the evaporator set downstream are contacted across a series of vacuum rotary drums (Figs. 32.8 and 32.9). The chemical residuals remaining in the pulp are diluted in this part of the process. Each stage of washing can achieve about 80% dilution of the chemicals, and three or four stages of washing are used to get to 99% ionic removal efficiency.

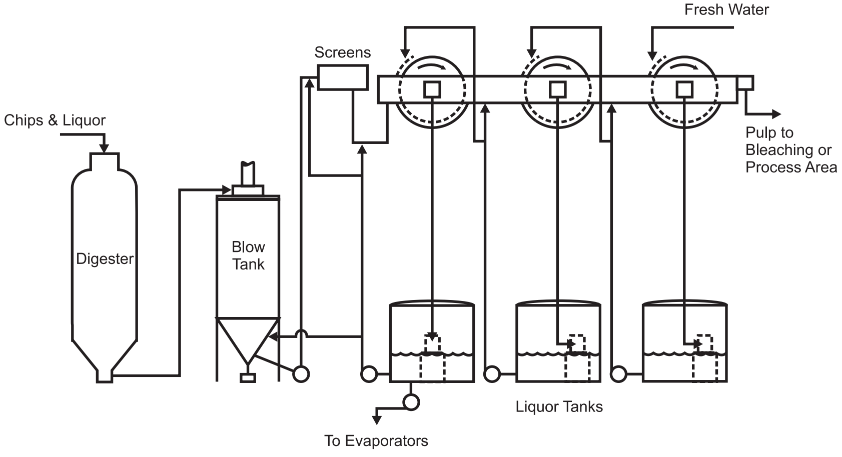


FIGURE 32.8 Diagram of a brown stock washing system.

FIGURE 32.9 Photograph of a brown stock washing system.

There are several mechanical, operational, and chemical factors that impact brown stock washer efficiency. The entrainment of air with the pulp can generate considerable foam, and the application of chemical defoamers to the process is quite common. Oil-based defoamers dominated this application for many years, but the global cost of hydrocarbon added to environmental concerns over volatile organic carbon (VOC) emissions from industrial sources has led to wide acceptance of silicone as the carrier solution for modern defoamer products. The replacement of oil-based by silicone-based defoamer products has resulted in improved cost-effectiveness and better paper machine runnability.

The pulp streams leaving the brown stock washers go on to either bleaching or directly to paper production, and a liquid waste stream called weak black liquor. Except for the cellulose fiber, the white liquor used as the cooking solution in the digester now contains all of the organics present in the original wood supply, so it is considerably darker in appearance. Since it has no further purpose in the paper production process, the weak black liquor can be thought of as a waste stream. Instead of disposing of the weak black liquor, paper mills embark on a process of chemical recovery, so that the chemical can be reconstituted for another pass through the digestion process. This process begins in a multiple effect evaporator set.

Evaporator Operation

The solids concentration of weak black liquor is increased by the evaporation of the accompanying water phase by heating the solution until the water flashes. This is done is a series of vertically oriented shell-and-tube heat exchangers, that have steam as the heat source on the shell side, and the concentrating black liquor on the tube side. Historically, the black liquor flow has been in an upward direction on the tube side of the exchanger, which is called rising-film operation. More recently, improved process efficiency has been realized with falling-film units, where the liquor flow is downward. As previously mentioned, black liquor concentration is conducted in a series of evaporation exchangers called effects, but steam from the powerhouse is only used in one, where the liquor reaches its highest concentration, usually around 55 to 60% solids (Fig. 32.10).

The evaporation is performed in a series of exchangers, so that they can be operated at different pressures, using the decreasing pressure as the chance to flash vapor from the remaining energy present in the condensate phases. The first effects (or the last effects, depending on the mill's numbering system for the effects) operate at greater than atmospheric pressure. However, the other end of the evaporator set is under vacuum conditions, so that even more water can be evaporated as the heating medium cools. This is an important energy savings aspect of the design, and allows for more pounds (kilograms) of water to be driven from the liquor than pounds (kilograms) of powerhouse steam are used. In fact, systems are operated to routinely achieve 4 to 5 lb (kg) of water evaporated from the liquor per pound (kilogram) of steam applied, and the most modern system will design for 6 to 7 lb (kg) of evaporation per pound (kilogram) of steam used. This concept of steam economy is very important to the cost-effective operation of the Kraft pulp process.

As the water is driven from the liquor, liquid condensate is formed in each evaporator body. This form of condensate has several

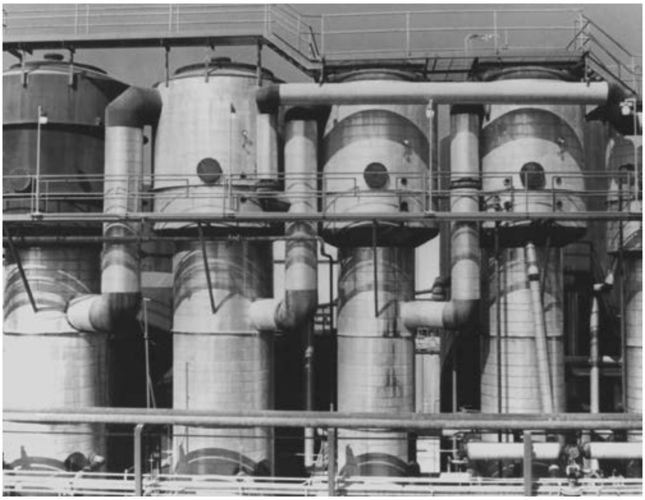


Figure 32.10 Kraft process multiple-effect evaporator set. (*Courtesy of HPD Corporation*.)

names: foul condensate, dirty condensate, or contaminated condensate. It is not pure enough to be returned to the powerhouse for use as boiler feedwater, but it has an important role in the process as the wash water used in the brown stock washers to dilute the concentration of cooking chemicals remaining with the pulp.

Depending on mill nomenclature, the first or last effect uses the fresh steam from the powerhouse. This condensate can be returned to the powerhouse for reuse as boiler feedwater, but only if certain precautions are taken to assure that the black liquor has not leaked into the low-ionic content condensate. The best practice is for systems to have in-line conductivity sensors on the condensate flow that trigger a diversion valve if a higher conductivity value is detected. An important design consideration is for the lag time between the conductivity sensor and the diversion valve to be less than the time it takes for the liquor to flow between the points in the systems. Most mills have their own individual horror stories about what happens to their systems, when a liquor leak occurs and the diversion system fails to operate. Therefore, it is becoming standard practice to have redundant capabilities, one located and maintained in the pulp mill area, and a second at the powerhouse as additional protection for boiler feedwater.

At the other end of the evaporator set is a condenser to extract the last heat content from the flashed vapor. Water conservation in this cooling application is accomplished by having a cooling tower service this condenser, but the frequency of process intrusions into the cooling water makes the operation of this tower very demanding. Since it is the purpose of the cooking chemical to help dissolve the wood chips in the digester, when contact is made with a cooling tower made from wood, a similar digestion process can occur. In addition, the organics that come along with the cooking chemicals offer a food source for microbial populations, which can be troublesome to both the tower and the performance of the condenser. It is necessary to monitor the structural integrity of cooling towers that service evaporator systems to be sure they are safe.

Cascade Evaporation

The solids content of liquor leaving the evaporator set is usually around 55 to 60%, but this is still below the desired threshold for burning in the recovery boiler. Therefore, an additional concentrating step is taken. In older recovery operations, this was done by contacting the black liquor with the flue gas from the recovery boiler in a device called a cascade evaporator. Cascades are in disfavor for modern mill operation, because they represent a fire hazard and because of the environmental challenge they cause in controlling odors emanating from the recovery process. A cascade evaporator can increase the solids content in the now concentrated black liquor, up to 65 to 70%, which is readily combustible in the recovery boiler.

Concentrator Operation

An alternate to the use of the cascade evaporator for extracting the final amount of water from the black liquor is called a concentrator. This unit looks very much like an additional effect in the evaporator set, and functions in the same way (Fig. 32.11). Concentrators can be designed to provide liquor solids up to 80%, which makes the combustion more efficient, since there is less energy required to evaporate the water present in the liquor. At this solids concentration, black liquor is quite viscous and hard to pump, but these are challenges that operating teams handle in exchange for the benefits they derive. Again, steam from mill headers is used as the heating medium in the concentrator, and precautions against contaminated condensate being returned to the powerhouse must be taken. As the liquor leaves the concentrator or the cascade evaporator, it is ready to be burned in the recovery boiler, a combustion unit unique to the Kraft process and the economic heart of this mill design.

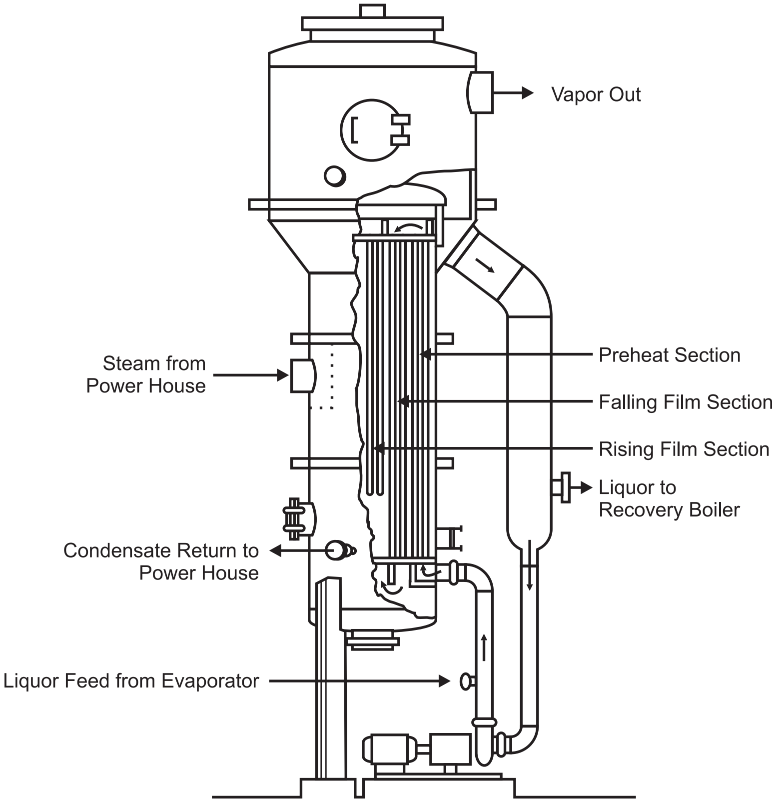


Figure 32.11 Black liquor concentrator.

Kraft Process Recovery Boiler

It is hard to imagine that any other piece of industrial equipment that does not touch the product being produced, in this case the sheet of paper or pulp, is more critical to the financial success or failure of the mill than the Kraft process recovery boiler. This unit performs two indispensable feats in an incredibly economical way. However, for these benefits, there are also unique challenges that must be faced and overcome in operating these units.

On the fireside, the Kraft process recovery boiler is unique in that its fuel is the concentrated black liquor that contains the spent chemicals from the digestion process. By managing the air input to this boiler, it is possible to begin the process of reconstituting the cooking chemicals, instead of treating them as a waste and discharging them to the environment. The organics present along with the cooking chemicals serve as the boiler fuel. Once the combustion process is in sustained operation, the recovery boiler can be generating 40 to 50% of the entire mill's steam requirement at zero purchased fuel cost. While this process was developed at a time when environmental impacts and energy costs were of less importance to the survival of the paper mill, the process has been optimized and improved over the years to become essential.

The concentrated black liquor is simply sprayed into the fireside of the boiler. Some drying occurs immediately, with the moisture going upward with the flue gas flow, and the inorganic cooking chemicals and the organic fraction of the wood falling to the bottom of the furnace. The lowest part of the furnace is maintained in an oxygen-deprived condition, so that the organics can keep burning. The process obtains oxygen from the sulfate ion present, reducing it to the sulfide ion form used in the digester. What develops at the bottom of the recovery boiler furnace is a liquid pool called smelt, molten sodium hydroxide and sodium sulfide. This liquid moves out of the furnace through several channels called smelt spouts, where it is combined with a large volume of water in the smelt dissolving tank.

One unique aspect of the recovery boiler fireside is how the air is managed. In normally fired boilers, the air required to provide oxygen for the combustion process is usually mixed in with the fuel to achieve the cleanest and most efficient burning. The recovery boiler segments the injection of air into three or possibly more separate systems. The primary air zone at the bottom of the furnace is closely monitored to limit oxygen in the smelt bed, so that the reduction of the sulfate fraction of the liquor is complete. A secondary air zone, higher in the furnace, provides sufficient air for final combustion of the organics, and the third or tertiary air injection system is used to assure environmental compliance is maintained. Old recovery boilers have a single forced-draft fan to provide the three air streams that are regulated by louvers or dampeners in the air flow path. Modern units have individual fans on the different air systems for more efficient control.

From a waterside perspective, the operation of the Kraft process recovery boiler is a lot like many other industrial boilers. These are often quite large units, and because of the fouling nature of the inorganic materials on the fireside, the unit heat input factors are quite low, minimizing driving forces that contribute to the accumulation of waterside deposits. The water volume of the boiler is large compared to the steaming rate, so chemical excursions of water chemistry occur more slowly, deflect the water chemistry to a lesser extent, and rebound from the excursion over a longer period. The modern design for a recovery boiler usually incorporates a very large economizer, so that maximum heat can be collected from the flue gas stream. The operation of these recovery boiler economizers is often a major problem for the mill. According to the Black Liquor Recovery Boiler Advisory Committee (BLRBAC), up to 40% of forced outages to these units are caused by economizer failures.

What makes the operation of the Kraft process recovery boiler so demanding is what can happen in the event of a waterside tube failure. With most other boiler designs, a tube failure requiring the boiler to be shut down can cause a loss of production and some increased cost for maintenance. However, water entering the smelt bed could cause a smelt/water explosion capable of causing severe damage to the unit. It is this concern regarding the potential for smelt/water explosions that causes this boiler design to be one of the most closely monitored in any industry. The reason the BLRBAC organization exists is that years ago explosions of this type were disturbingly common. Explosions cause a huge financial hardship for the mill as well as serious safety hazards that includes deaths. In many cases, paper corporations will not rebuild failed boiler systems, causing permanent mill shutdown. As shown in Fig. 32.12, the incidence of these events is now rare.

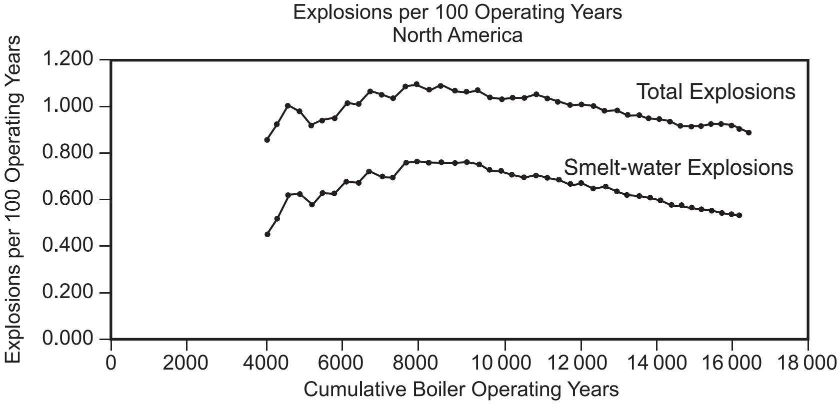


Figure 32.12 BLRBAC data documenting recovery boiler operating incident rates. (*Courtesy of BLRBAC.*)

Because of this possibility of an explosion resulting from what would otherwise be a routine part of boiler operation, water treatment for recovery boilers receives special attention. In some mills, higher-quality water is segregated for use in the recovery boiler. Chemical treatment selection gets special attention, and boiler waterside inspections are conducted with increased intensity. It is common for tube specimens to be cut from areas in the lower recovery boiler furnace, where the heat input is the highest and where deposits are most likely to develop. Some paper corporations have strict guidelines requiring that they chemically clean their recovery boilers after five years of operation, despite the absence of any indication that deposits are accumulating at a rate that would cause overheat failures. It would be very rare for any company operating a recovery boiler to attempt to clean the boiler while in service, since deposits coming off the surfaces could either preferentially accumulate in the hottest areas, or could bridge across a tube opening and cause a short-term overheating failure. Because of the intense scrutiny that these units receive, which is appropriate for their importance to the mill, water system failures are quite rare. This is a compliment to the science of water treatment that has been fully utilized in this critical aspect of mill operation, and the dedication of the crews that work on these units on a daily basis.

Smelt Spouts

There are several troughs at the bottom of the recovery boiler that allow the smelt to be conducted into the smelt-dissolving tank, where it can be more fully prepared as the cooking chemical for the Kraft process another time. The most common spout design has an internal cooling water path than maintains the metal temperature in a protective range. One issue that can arise is that the metal can get too cool, causing the smelt to congeal, a process called “jellyrolling.” This is avoided by having both minimum and maximum temperature controls on the smelt spout cooling water system. It is an operating practice that these spouts are simply discarded after one year of service. There is a small but growing number of so-called dry spouts on the market that use advanced refractory materials, and thus do not require the same cooling water system. A common operating problem with recovery boilers arises when one or more spouts become plugged by frozen smelt. An uncontrolled “rush” of smelt that occurs when a plugged spout is reopened has caused more explosions since 2002 in the smelt-dissolving tank, than the classic smelt-water reactions inside the recovery furnace area.

Smelt-Dissolving Tank

As the smelt leaves the smelt spout, it is contacted by a large flow of water, which quenches the molten smelt and dissolves the chemicals as ionic salts. This solution falls into the smelt-dissolving tank. Some rumbling is a normal occurrence, although tanks have been bounced off their foundations by larger events. At this point of the process, the dissolved smelt has a greenish tint due to contact with steel materials of construction, and it is called green liquor. Once formed as green liquor, this chemical solution leaves the recovery boiler area, and enters the recausticizing process.

Recausticizing Process

The recausticizing process is a three-step procedure, with several recycle loops associated with each step. The process description provided here will not get the depth of attention as the other parts of the Kraft process. However, this area has a significant impact on mill performance.

Green Liquor Clarification The green liquor clarifier (Fig. 32.13) receives the green liquor from the recovery boiler, and serves to collect undissolved solids called dregs that would cause operational problems downstream in the recausticizing process. A suspended solids concentration in the green liquor coming to the clarifier of about 1000 mg/L (or 0.1% of total flow) is typical. An anionic flocculant is

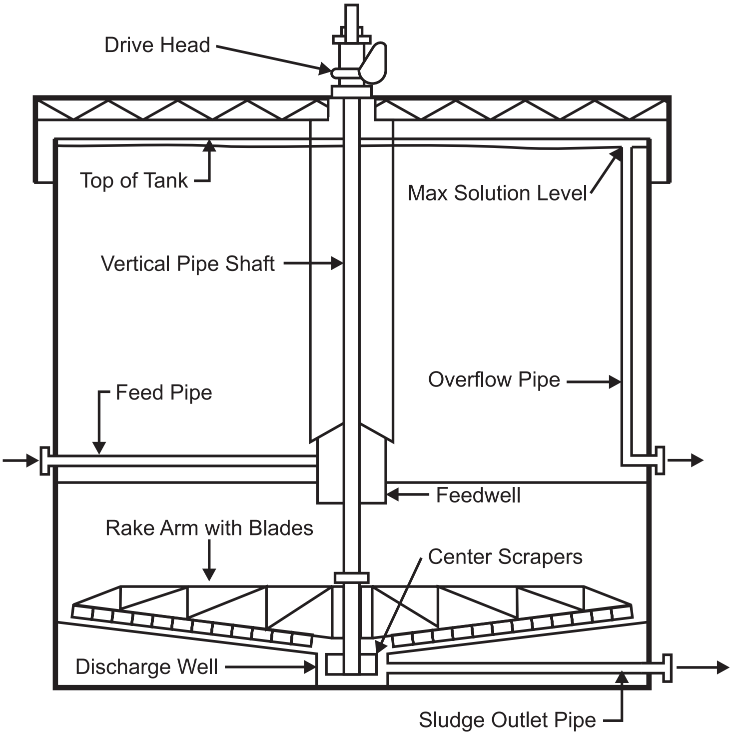


Figure 32.13 Green liquor clarifier.

often used to enhance settling of the dregs, resulting in a final concentration of 70 to 80 mg/L in the clarified liquor. This represents 92 to 93% removal efficiency. The dregs from the bottom of the green liquor clarifier are washed by a liquid stream, resulting in some weak liquor that is added to the smelt-dissolving tank.

Causticizer The formal conversion of green liquor to the white liquor used for chip digestion occurs in the causticizer system. Green liquor and pebble lime coming from the lime kiln feed the causticizer, where aggressive agitation results in the hydration of the calcium oxide (CaO) chemical form of pebble lime to slaked lime [$Ca(OH)_2$]. Slaked lime is needed to undergo a chemical reaction with sodium carbonate present in the green liquor, which is ineffective in the digestion process. The resulting reaction forms insoluble calcium carbonate, which is separated from the white liquor in the white liquor clarifier, and then goes to the limekiln to be converted back to pebble lime. The water solution in the causticizer is hot, and gets hotter because of the exothermic reactions that occur. This improves calcium carbonate removal, since this molecule, unlike many others, is less soluble in higher temperature solutions than cooler ones. Causticizers are essentially mixing vessels, and a series arrangement is used to promote the chemical conversions. A slight excess of lime (about 1–2%) promotes causticizing efficiency, but too much can hamper solids removal in the white liquor clarifier.

Lime Kiln Many mill engineers have sought refuge from cold weather conditions under the lime kiln. A limekiln is a slightly inclined rotating cylinder, nearly horizontal to ground. Inside the cylinder, the calcium carbonate slurry from the causticizer is exposed to a heated combustion gas stream. Most lime kilns use natural gas as the heating source, but a few are now using petroleum coke and other by-product fuels to operate at lower cost. As the slurry heats and dries, the chemical composition changes, according to this reaction:

$$\mathrm{CaCO_3\ slurry} \xrightarrow{\text{heat}} \mathrm{CaO}\downarrow + \mathrm{CO_2}\uparrow + \mathrm{H_2O}\uparrow \qquad (32.1)$$

The conversion efficiency of the lime kiln is in the range of 90 to 94%. Higher conversion efficiency and a smaller particle size of lime are produced using chains inside the kiln, mostly toward the dry end. The chains do nothing more than flop around as the kiln rotates, literally bashing the particles into a granular form. One operational problem that occurs in lime kilns is the formation of rings, which blocks the flow of the lime particles down the kiln. Some kilns have wet scrubbers on the outlet flue gas stream, to collect the smallest lime particles that are entrained along with the gases. The presence of calcium salts from the kiln makes chemical treatment of this system demanding, even when the water supply is high quality.

White Liquor Clarifier The calcium carbonate precipitates formed in the causticizers are separated from the ionic sulfide and hydroxide salts in the white liquor clarifier. Clear white liquor is needed for the digestion process to avoid contaminating the pulp, which makes subsequent bleaching to produce white paper grades more difficult and costly. A clarifier similar to the green liquor clarifier is used, operating at rise rates of 1.6 to 1.8 ft/h (0.49–0.55 m/h). Some mills making higher-quality pulp use a polishing filter following the clarifier to ensure maximum liquor clarity. The precipitates are called lime mud, since the solids content is 35 to 40%. The lime mud is pumped through two stages of washers and filters and inventoried in a storage tank. The lime mud is the feedstock for the lime kiln, which was discussed previously.

The clear white liquor leaving the white liquor clarifier is the primary chemical additive used for the digestion of wood chips in the digestion process, discussed earlier.

Chemical Pulping—Non Kraft

Historically, several chemistries over a range of solution pH values have been used to chemically remove the cellulose fibers from the other components present in the wood chips. Currently, the Kraft process (discussed earlier) dominates the chemical pulping processes. Here, the other chemical pulping processes will be discussed to add some historical context to current operating practices.

Chemical pulping is based on a compromise; the longer the chips are cooked, the higher the resulting fiber yield, but the longer the chemicals involved in the process are exposed to the fibers, the weaker the fibers become. Therefore, close monitoring of the chemical cooking process in terms of the chemistry, temperature, and contact time is required. Before the late 1980s, most pulping operations were conducted in an acidic environment, usually based on salts of sulfur. This was efficient, but the resulting paper had a limited lifespan, since the acidic remnants left in the sheet degraded its structure over time. In addition, the acidic conditions limited the ability to use calcium carbonate filler materials because the acid and the acid-soluble carbonate filler materials are incompatible.

The use of nonfiber filler in the sheet affects the process in two beneficial ways:

1. Nonfiber filler is cheaper than wood fiber, and the cost of materials is reduced.
2. Fillers can dramatically improve the print quality of the sheet, and they are used in many graphics-related paper products.

One of the sulfite pulping processes still in some use is based on the ammonium sulfite chemistry, which is known as the Red Liquor cook. Like the Kraft process, the Red Liquor process features a recovery boiler, although the design and operating parameters are quite different from the Kraft process recovery boiler. Instead of forming a molten smelt pool in the bottom of the recovery boiler furnace, the Red Liquor recovery boiler recovers the cooking chemicals as a fume, in the gaseous state. As such, there is not the same hazard of a smelt/water explosion, but working in the area of a Red Liquor recovery boiler has its own hazards. The occasional release of gases from the boiler requires personnel working in the area to have on their person an escape respirator mask, should the surrounding air become too toxic.

Recycled Pulp Production

While it is not practical to substitute recycled fiber for all virgin fiber used in paper production, increasing the amount of recycled fiber has a number of financial and environmental benefits.

Deinking and Secondary Fiber Use

A major component of the modern environmental movement has been the push to reduce the harvesting of trees as a source of fiber for paper, relying instead on the recycling and reuse of paper as the feedstock for papermaking operations. Secondary fiber (as compared to trees, which would be the primary source) can come from several sources: industrial, commercial, or the result of municipal recycling programs. There are a number of different types of recycled paper, each having its own acronym:

- Old corrugated containers (OCC)
- Old newsprint (ONP)
- Mixed office waste (MOW)
- And many others

The challenge in using recycled fiber as a source of paper is the management of contaminants that can be reasonably expected to be present, such as printing inks, and those contaminants that are highly variable and unexpected. Traditionally, it has been assumed that all detrimental substances that must be overcome arrive with the waste paper. Inks, dirt, and stickies, which are adhesive contaminants originating from wood pitch, white pitch, fillers, etc., have all challenged the equipment and chemistries of effective deinking. However, more recently, water quality in deinking mills has become an increasingly important factor in controlling, and in certain cases, eliminating detrimental materials found to inhibit the brightening and bleaching objectives of every deinking mill.

Incoming waste paper carries with it the seed for the catalase enzyme. Catalase control and elimination has become a primary concern of any deinking mill needing hydrogen peroxide to be effective. Catalase is a detrimental enzyme that attacks and reacts with peroxide. This leaves less peroxide available to bleach the fibers in any bleaching stage (at the pulper, disperser, or at a bleaching tower). Catalase also persists throughout deinking mills in the water loops. The treatment of catalase can only be done in the water circuits, and an in-depth knowledge of dilution and consistency control is essential for treating this problem.

Flexographic ink is another contaminant problem that is most effectively handled through water clarification. Also called flexo ink, it is a water-based ink with an extremely small particle size, too small to be effectively removed through flotation operation. With the removal of almost all deinking wash operations (deckers or washers) and their subsequent replacement with flotation processes, the water clarification loops remain the most effective place in a deinking mill to remove flexo ink.

On its most fundamental level, the deinking of waste paper requires detachment followed by separation of ink, dirt, and stickies from usable fiber. Once this occurs, it is the job of the water circuits in the mill to prevent the re-attachment of any of these detrimental substances back onto the fiber. Every unit operation in a deinking mill that separates ink, dirt, and stickies presents a secondary problem in how to treat the effluent from that specific unit operation. Sewering the entire effluent stream is not feasible in all cases, as the yield of any deinking process is what benchmarks it as financially viable or not. This requires the water loops to be cleaned of detrimental substances without removing the fines and short fiber that contribute positively to the yield.

Oxidative Bleaching (P Stage)

Pulper chemistries continue to focus on ink detachment, and the best pH condition continues to be on the alkaline side. Traditional alkaline chemistries using hydrogen peroxide, sodium hydroxide, sodium silicate, and surfactant are used to swell the fiber, detach the ink, and reverse the alkali darkening process, normally created by the high pH conditions.

Reductive Bleaching (Y Stage)

Reductive bleaching has been more common as both a color stripper and a final brightness enhancer before going to the machine process. Hydrosulfite, direct borohydride injection (DBI), and formamidine sulfinic acid (FAS) are used in various deinking processes with a 1 to 3 point brightness increase being gained from their effect. If a 1 to 3 point brightness increase enables a mill to move into a more value added grade, these technologies are sometimes more cost-effective than buying brighter waste paper or installing a bleaching tower or other brightening unit operation. One drawback of some of these technologies, however, is their interaction with certain microbiological control programs.

Neutral/Near Neutral (pH = 8.0)

Limited success has been found with neutral or near-neutral pulping chemistries. The cost benefit of a near-neutral chemistry should be evaluated against the decrease in quality that occurs from the absence of a bleaching agent, and more effective ink detachment seen in an alkaline process. In many cases, a remedy should be added at the end of the process to make up for the savings realized from the near neutral technology. Much effort continues to be put toward finding more effective neutral or near-neutral pulping programs. Alternatives to both alkaline and near-neutral chemistries have started to be evaluated using enzymes and silicone-based products. Their effectiveness compared to the most recognized alkaline alternative has yet to be established.

Equipment Innovations

The two major changes in deinking mill operations are the introduction of the drum pulper and the flotation cell.

Drum Pulper Many times, a stickie particle will start in a process as a full sheet of plastic, before being twisted and disintegrated as it moves through the process. A typical batch pulper is positioned vertically, resulting in a high shear rotor and heavy fiber-to-fiber interaction. This high shear action creates a detrimental condition in terms of plastic disintegration into stickies. The smaller a stickie is, the harder it becomes to remove from the process.

The drum pulper, in comparison, is horizontally oriented and uses gravity to allow the fiber-to-fiber interactions to take place. This is a much more passive method of detaching the ink, dirt, and stickies, and allows stickies to remain in their larger forms, which makes them easier to remove.

Flotation Flotation technology came from the mining industry. Its concept allows for detached ink, which is hydrophobic in nature, to attach itself to a rising bubble in a flotation cell. The cell is designed to allow the bubbles to collect as froth at the top of the cell and be removed. The treated pulp goes forward in the process.

Flotation technology saw a dramatic improvement in yield. Flotation increased the process yield from a low of 60% to a much better 80% yield. This had a positive impact on the economics of operating a deinking mill, as an alternative source to virgin fiber.

In the early part of the 21st century, the heavy exportation of waste paper to supply the increasing Asian demand tightened the North American waste paper market. It is expected that continued tightening would increase the contaminant loads in available waste paper, demanding new and improved chemistries and equipment throughout the world.

Pulp Bleaching

If a paper mill's final product is a white grade of paper or paperboard, bleaching of the pulp is done in the pulp mill. Unbleached brown stock from the digesters is treated with chemical agents to increase brightness and give it a whiter appearance. Bleaching is accomplished by delignification, brightening of the unbleached pulp, or both. Delignification is the chemical removal of residual lignin from the pulp. Lignin absorbs light and gives unbleached pulp its brown color. Brightening simply involves a chemical alteration of those portions of lignin that impart the color so that they no longer absorb light. To produce high-quality, optically stable pulps, bleaching methods that delignify the pulp must be used. This is normally the case with chemical pulps, such as Kraft or sulfite pulps, where high brightness levels are required. With mechanical pulps, where a maintaining high pulp yields through preservation of the lignin is critical, brightening is the preferred bleaching process.

With chemical pulps, bleaching is usually achieved through a sequence of three or more process stages, each utilizing different chemicals and conditions depending upon its specific purpose. The unit operations for each stage normally include mixing, reacting, and washing. Sequences and associated process equipment can vary considerably from mill to mill, depending on the final product requirements, capital and operating cost considerations, and environmental factors.

Each different bleaching stage has been assigned an abbreviation or shorthand notation, so that sequences can be more easily described. The common bleaching processes and abbreviations include:

- C—chlorine bleaching using chlorine gas (Cl_2)
- D—chlorine dioxide (ClO_2) bleaching
- E—caustic (NaOH) extraction bleaching
- H—chlorine bleaching using sodium hypochlorite (NaOCl)
- O—oxygen (O_2) bleaching
- P—Hydrogen peroxide (H_2O_2) bleaching
- Z—ozone (O_3) bleaching

In some cases, multiple chemicals are used in a single stage, for example, caustic, oxygen, and peroxide. In the shorthand notation, this would be written as EOP or E+O+P to show that the three chemicals have been combined in a single bleaching stage. Repeated stages used to achieve higher brightness are noted by adding subscripts, such as D_1, D_2, and so on.

Figure 32.14 is an example of a typical five-stage bleaching sequence, identified by the shorthand notation $D_{100} - E_{OP} - D - EO - P$.

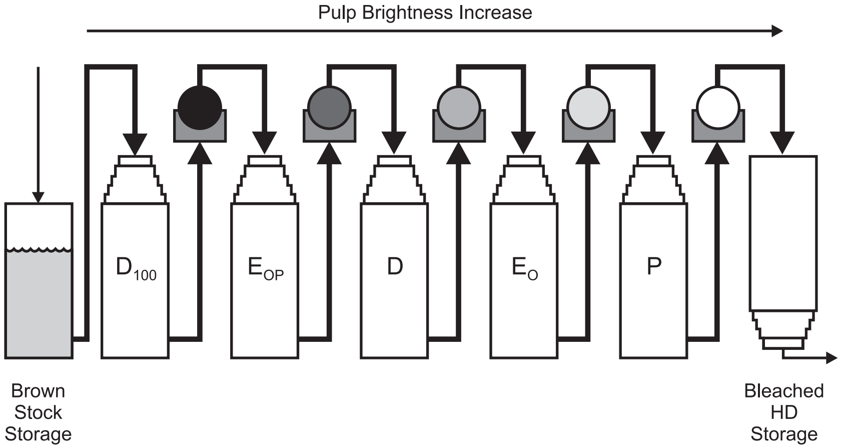


FIGURE 32.14 Typical five-stage bleaching process.

In this example, chlorine dioxide (D) is used in the first, and third, stages. The second stage uses caustic soda (E) for extraction of residual lignin from the pulp. This particular extraction stage also utilizes oxygen (O) and hydrogen peroxide (P) to assist in bleaching, initially in combination with caustic, and with a final hydrogen peroxide only stage.

The first two stages of a bleaching sequence usually accomplish most of the delignification. Chlorine dioxide (ClO_2) is a powerful oxidizing agent, which reacts rapidly with lignin under acid conditions in the first stage, while affecting the carbohydrate fraction very little. The following extraction stage then solubilizes the lignin, rendering it susceptible to removal by the alkali and good washing. Caustic soda (NaOH) creates the strong alkaline conditions present in the extraction stage. This extraction stage also reactivates the pulp for further oxidation in the following stages. Oxygen (O_2) and hydrogen peroxide (H_2O_2) are sometimes added to the extraction stage, where they react selectively with the remaining lignin in the pulp, reducing the requirement for more expensive chlorine dioxide in the following stages.

The chlorine dioxide stages are often referred to as brightening stages, since the greatest gains in pulp brightness are achieved here, although removal of the final traces of lignin continues to take place in both stages. The specific operating conditions of time, temperature, chemical charge, and pH in the D_1 stage are established for the efficient bleaching of undesirable shives (dark fiber bundles) that may be present in the pulp.

In some cases, a second extraction (E_2) stage may be found between the final two D stages. If needed, a dechlorinating agent, such as bisulfite, may be used at the final D stage washer to control excessive chlorine dioxide residuals in the fully bleached pulp.

The process equipment depicted in Fig. 32.14 is typical of many bleach plants. However, as with sequences, specific process equipment can vary widely from mill to mill. In the example sequence, bleaching chemicals and steam (used to control the temperature of each stage) are applied to the pulp through mixers located immediately before a reaction tower. Good mixing is critical to achieve efficient bleaching. Bleach towers are normally tall cylindrical tanks, which provide the appropriate retention time for the specific bleaching reaction of each stage. Pulp discharged from a tower is then washed to remove as much of the spent chemicals and soluble reaction by-products as possible. Washing is important, since excess residual materials carried along with the pulp can interfere with the efficiency of the following stages. Hot water and machine whitewater are usually used in combination as shower water on the final bleach stage washer. Some sort of counter-current washing configuration, utilizing filtrates from each stage, is usually used throughout the remainder of the bleach plant, to achieve the greatest reduction in freshwater usage, and to minimize effluent discharge volumes. Rotary drum vacuum filters are the most common type of equipment used for washing in the bleach plant. However, other washer styles are in use across the industry, including compaction baffle pressure filters, wash presses and atmospheric diffusers to mention just a few.

The sequence shown in Fig. 32.14 is one of a variety that is referred to as elemental chlorine free (ECF) bleaching sequences. Most bleach plants now use some type of ECF sequence. Elemental chlorine in the form of chlorine gas, or in solution as hypochlorite, was used in most bleaching sequences until the 1990s. These were low-cost and effective bleaching agents, but were subsequently found to be major contributors to the formation and discharge of chlorinated organic compounds, including dioxins. Hypochlorite was also found to play a part in the generation of chloroform from bleach plants. Consequently, chlorine and hypochlorite have been eliminated almost entirely from the bleaching of pulp. They have been replaced by chlorine dioxide or other bleaching chemicals that react differently and form fewer undesirable by-products.

A few mills, primarily in North America and Scandinavia, have gone a step further to employ totally chlorine free (TCF) bleaching. The elimination of all chlorine containing chemicals for bleaching, including chlorine dioxide has led to the development of TCF bleaching sequences that use oxygen, ozone, and peroxides. Higher costs and uncertain incremental environmental benefits have limited more widespread adoption of TCF bleaching. Both TCF and ECF sequences may also supplement other novel treatments such as enzymes, chelants, and peracids.

As an environmental enhancement to the bleaching process a form of oxygen bleaching, usually referred to as oxygen delignification has become quite common across the industry. The oxygen delignification process is placed between the digesters and the bleach plant. Oxygen is used under alkaline conditions, along with elevated temperature and pressure, to reduce the lignin content of unbleached pulp by about 50% before the bleaching process. This dramatically reduces the amount of chlorine dioxide required for delignification in the bleach plant. In addition, unlike most bleach plant filtrates, the filtrate generated by oxygen delignification is very compatible with the Kraft chemical recovery system, thus reducing effluent discharge.

Another interesting pretreatment option to reduce the use of bleaching chemicals is the use of an enzyme ahead of the bleach plant. One specific enzyme treatment can reduce the amount of chlorine dioxide required for delignification by as much as 15 to 20%. The enzyme functions by solubilizing organic complexes in the pulp, allowing the lignin to diffuse more easily from the fiber in the following D stages. Being natural proteins, enzymes require a very narrow range of temperature and pH to work effectively.

As mentioned before, except from TCF sequences, bleach plant filtrates cannot be recovered like brown stock filtrates to be burned in the recovery boiler. Chlorides present in the bleach filtrates are incompatible with recovery boiler metallurgy, and would ultimately result in costly, even potentially catastrophic equipment failure. Only limited success has been achieved thus far in efforts to treat ECF filtrate streams to remove these chlorides, (or to segregate nonchloride containing portions of bleach filtrate streams) in order to accommodate chemical recovery of the bleach plant waste streams. Consequently, in the vast majority of cases, bleach plant filtrates are still sent to a wastewater treatment facility, after their use in counter-current washing on the bleach washers.

Due to the alkaline nature of most of the chemical processes involved, bleach plants are often susceptible to scale formation. This can negatively affect equipment performance, bleaching efficiency, and operational uptime. Scaling becomes even more pervasive, whenever efforts are made toward water conservation or closure of the bleach plant. The most common types of scale found in the bleach plant include calcium carbonate, calcium oxalate, and barium sulfate. If operating conditions that favor deposition of scale cannot be controlled adequately by normal process changes, chemical treatment with scale inhibiting compounds can be very effective in reducing or even eliminating scale problems.

Mechanical pulps, unlike chemical pulps discussed above, are normally bleached by brightening methods that do not remove appreciable amounts of lignin. The most common chemicals used for this purpose are sodium hydrosulfite ($Na_2S_2O_4$) and hydrogen peroxide (H_2O_2). Unfortunately, none of the bleach treatments provides a brightness gain that is completely stable on exposure to light and air. This results in the potential for a higher degree of brightness reversion (yellowing), with paper produced from bleached mechanical pulps as compared to bleached chemical pulps. This yellowing effect can be observed if a newspaper is left in the sunlight for a day, and the exposed surface is compared to any sheet in the same paper that did not experience direct sunlight.

Stock Preparation

The final steps in preparing pulp to be made into paper occur in the stock preparation processes. Refining is a very important function that has a major impact on final paper sheet performance. Pulp cleaning removes contaminants from the pulp stream, which could cause operational issues if allowed to come onto the paper machines. Stock dilution to the desired consistency occurs, in a series of tanks or silos that are most often called chests by those in the industry. In addition, the run of piping that goes from the stock preparation area to the paper machine is a location where process additives are routinely applied, and there are considerable water and energy savings to be obtained if advanced strategies are applied to this seemingly mundane part of the process.

The refining that occurs in the stock preparation section is not to be confused with the same term used in the development of mechanical pulp grades. In the stock preparation area, refining refers to the scuffing or abrading of the individual paper fibers, so that they will form properly on the paper machine. This process has also been called “beating,” and in those mills that apply this term, the refining process step is said to occur in the Beater Room. Two refiner designs are widely used: the conical design and the rotating disc. Both designs cause the fibers to rub against one another and metal surfaces in close tolerance conditions, creating individual fiber strands that can be best arranged on the paper machine.

The downside of refining is that a certain fraction of the fibers are cut or damaged in the process. This limits the number of times a given paper fiber can be recycled, since it will eventually get too short to provide adequate sheet properties. One paper manufacturer reports expecting to waste 35 to 40% of the recycle paper it buys, since the MOW paper it uses as a source of fiber, often contains a higher fraction of paper that has already been reused. The lesson here is that there can never be 100% recycling of paper, since the refining steps cause damage to the fibers as a by-product of preparing them for the final production steps.

Pulp contaminants going to a paper machine can cause any number of operational problems. Therefore, the pulp contaminants are removed to the greatest extent possible in the final stages of stock preparation in a series of screens and cleaners. Mills using recycled paper as feedstock require considerably more cleaning due to the presence of a number of foreign materials. Initial cleaning is accomplished through a series of sieves and strainers, with the openings sized to accept the target fiber size and reject larger objects. More intensive cleaning is accomplished in a series of centrifugal cleaners, where the pulp is spun in a circular manner. The heavier or denser contaminants are forced to the outside of the cylinder, while cleaned pulp is withdrawn from the center. It is difficult to size a single centrifugal cleaner to handle a large volume of pulp. Consequently, multiple centrifuge units are bundled onto a single bank, and larger facilities have a number of centrifuge pumps to handle the mass flow of pulp needed for eventual production. As is the case in the refining step, water exits to rejects or sewer. Recovery of this water ultimately occurs at the screw press where sludge is produced.

Stock storage ahead of the paper machine is a necessary step to provide the proper ratio of fiber and water going to the paper machine, and to maintain an inventory of fiber ready for conversion into the final paper sheet. When most papermaking was conducted under acidic water conditions, large tiled silos were the norm. Even if the tiles were acid resistant, the grout in between the tiles would degrade over time, requiring these chests to be rebuilt periodically. Despite having some internal mixing capability, these stock chests are never homogeneous, and problems can develop with stock spoilage from proliferating microbiological forms. Biocides are applied to prevent the microbes from reaching damaging population levels. Occasionally, studies will be done to determine the average retention time for stock in these storage chests, using nonreactive chemical additives that can be detected at very low concentrations. This determines if adequate mixing is occurring in the chest, or if some mechanical or operational changes are required.

A last piece of equipment before the paper machine is the fan pump. The purpose of the fan pump is to provide consistent slurry of water, chemicals, and fiber to be made into the paper sheet. A chemical feeding process improvement developed by Nalco in 2006, allowed the seemingly mundane task of adding polymeric retention, drainage, and formation chemicals to the stock as it flows toward the paper machine, to be a major water and energy savings opportunity. The previous practice had been to add polymeric material through a basic tee into the process line and assume that adequate mixing and dispersion was achieved. Using computational fluid dynamics modeling, Nalco scientists determined that an improved polymer mixing and distribution system could be developed. Whereas previously freshwater was used to mix and distribute the polymer, the innovative process allowed recycled process water to be used for this purpose. This development results in significant water and energy savings, since freshwater would have to be heated in the process. Improvements in polymer efficacy are also observed using this process, but the energy and water savings are the paramount benefit. One such installation resulted in reduced water usage of 200 gpm (45 m^3/h), and a reduction of boiler steaming rate of 8600 lb/h (3900 kg/h), due to recycled water being used for polymer mixing.

Paper Machine Operations

The objective of all unit operations discussed thus far in this chapter has been to create a water slurry of fiber and chemicals that can be formed into a sheet of paper desired by the marketplace. That process occurs on the paper machine, and it is a marvel of chemical and mechanical engineering. Using a newsprint grade paper machine as an example, the objective is nothing more than converting a bulk solution which contains 99.5% water, about 0.5 % fiber, and some chemicals, into a consistent sheet of paper 0.003 inches [3 mils (76 μm)] thick, at 60 mph (97 km/h), and at an economic price with minimal waste generation. Most paper machines operating in the early part of the 21st century are Fourdrinier and gap formers designs. A few older machines that make heavier, board grades of paper are called Cylinder machines.

Paper Machine Headbox

The Fourdrinier paper machine design starts at the headbox, as shown in Figs. 32.2 and 32.15. The headbox may be open to the air, in which case the furnish is gravity fed onto the paper machine, or the headbox may be pressurized. Some grades in the packaging segment, feature multiple layers or plies of paper, requiring multiple headboxes to distribute the furnish. One grade that is a particularly good example of this is the so-called White Top Liner often used in folding box board and other packaging materials. Strength and economy comes from the unbleached or brown layers, while improved printability and

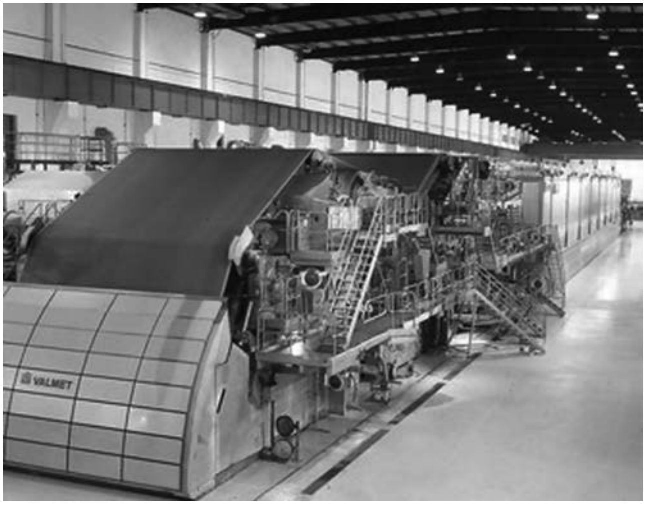


Figure 32.15 A modern Fourdrinier paper machine. (*Photo courtesy of VALMET.*)

customer appeal are derived from a bleached paper top layer. Multiple headboxes can be present in this design. The purpose of the headbox is to convert the cylindrical flow of fiber, water and chemicals into a planar flow on the wet end of the paper machine. Sometimes, inorganic scales accumulate in the approach piping and headbox, due to calcium or barium precipitation. Unless they are excessive, these deposits are tolerated during operation, and then cleaned off during periodic maintenance shutdowns.

Paper Machine Wet End

The 0.5 to 1.0% fiber content paper slurry is physically unstable as it emerges from the headbox, so it is spread onto a support structure called "the wire" as it begins its fast journey down the paper machine. Originally made of bronze, wires are now universally made of a plastic weave, so that water can freely drain away as the fibers get organized into a sheet. This wet end of the paper machine (Fig. 32.16) is also called the table area, and is characterized by a flat linear run. Removal of large amounts of water occurs easily at the wet end of the paper machine, enhanced by several mechanical features. After a brief span of free water drainage, more water is extracted by passing the wire over a series of foils, like inverted airplane wings that cause a vacuum gradient, to suck more water from the forming sheet.

Further down the table, the wire passes over a series of vacuum boxes, again with the purpose of sucking water easily from the sheet. The vacuum is created by a series of large, liquid-ring vacuum pumps or blowers.

Some mills pass the wire under a steam box arrangement, designed to heat the water/fiber slurry and encourage water drainage by lowering the viscosity of the water component on the sheet.

FIGURE 32.16 Photo of a large Fourdrinier wet end.

The use of steam boxes is typically an expensive approach for water removal, and consideration of other benefits is a must to substantiate the investment. The Couch Roll is located at the end of the paper machine wet end where the sheet is separated from the wire for entry into the press section. At this point, many paper grades are up to 25% fiber, meaning that 95% of the water that left the headbox has been taken away from the sheet. Given that the means of water removal further down the paper machine costs more, effective water removal in the wet end is extremely important to the cost-performance of the paper machine.

A water stream is used to establish the width of the sheet as it is formed on the wet end of the paper machine. As it leaves the headbox, the water/fiber slurry tends to spill out to the side of the wire, until it achieves some dimensional stability. This results in a few inches (centimeters) of the sheet on both sides that will not meet the thickness specification of the grade being produced and that needs to be removed as early in the process as possible. This is accomplished by spraying water along the edge of the sheet as a knife, cutting the thinner paper. This water stream is sprayed through nozzles called the trim squirts. To achieve the cutting effect on the edge of the sheet, high-pressure water also known as shower water is squeezed through small tolerance openings in the nozzles, making water quality very important to the performance. Water not containing fiber or process additives, typically freshwater or recovered condensate, is usually used for this purpose. In addition, shower nozzles require periodic replacement, use of hard material or cleaning because of water high in hardness content that will form scale and wear from high velocity.

Water issues can affect the performance of the paper machine wet end in several ways. Manganese is an element found in many water supplies at a concentration of 50 μg/L or higher. The presence of manganese in the stock dilution water has been observed to form a stain-like deposit on the plastic wire that supports the water/fiber slurry. While primarily a cosmetic issue, because the manganese forms a characteristic black deposit on the white wire, the thickness of the manganese deposit can retard water removal. In addition, the water recovered from the paper in the wire pit under the wire is a classic breeding ground for microbiological organisms. The presence of organic contaminants in the incoming water has been shown to be a food source for the organisms present. By doing a better job of extracting organic contaminants from the incoming water, one mill demonstrated a 50% reduction in sheet web breaks, resulting in an annual savings of $1.1 million.

Polymeric chemical additives are fed to paper machine wet ends to enhance water removal from the sheet and retain small particulates. These are often called RDF chemical programs, speaking to improvement achieved in retention, drainage, and formation. Some mills, often in the board grade segment, operate mill water systems as zero liquid discharge (ZLD) so that no water is discharged from the process in liquid form. Ionic concentration of the circulating mill water under this operating strategy is very high, and inhibits the ability of the polymeric additives to uncoil, interfering with the polymers adsorption onto the fiber surface and performance to meet functional properties such as strength. This impact decreases the benefits that could be achieved under more normal water chemistry conditions. Special care must be taken in RDF chemical additives selection, when advanced water recycling practices are utilized.

Paper Machine Press Section

Anyone familiar with an old wringer-style clothes washer in operation will readily understand the operation of the paper machine press section. By taking the sheet, which is supported by a water absorbing fabric called a felt, between a series of rolls, water is squeezed from the sheet. This part of the process increases fiber solids in the sheet from 20% to upwards of 55%. This represents nearly 17% of the water associated with the sheet as it leaves the wet end of the paper machine.

The point at which the press rolls form a narrow passage through which the sheet must pass is called a nip, and this is where water removal by mechanical force takes place. A standard press section involves the sheet passing through three nips, as shown in Fig. 32.17. Water removal in the press section is slightly more expensive than in the wet end area, but far cheaper than evaporation, which occurs in the paper machine dryer section. Sheet consolidation and compaction occurs as a result of passing the sheet through the tight nip tolerances in the press section. In some grades, those that require greater strength, this can provide a considerable benefit.

The press section area features a vacuum section to enhance water removal. This system is comparable to what is used on the wet end of the paper machine, but instead of sucking water from the sheet

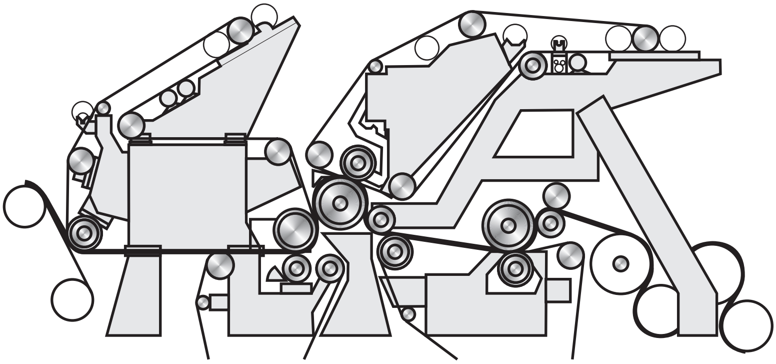


Figure 32.17 Standard three-nip press section.

through the wire the vacuum system in the press section functions by sucking water from the felts to allow more efficient water wicking from the sheet.

A major factor in effective press section performance is the cleanliness of the felts that support the sheet. Felts that become filled with fiber, organic deposits, or inorganic materials cannot pass water as efficiently. Felt cleaning is an important component of optimal press section performance. It is important for the operations team to understand the nature of their specific felt cleaning requirement, so that effective chemical additives can be applied. Deposits based on organics might require a solvent-based cleaner, whereas inorganic deposits require an acidic cleaning solution. Mills must decide if press felts require continuous cleaning, cleaning during a down, or batch cleaning while the machine stays in operation. This decision is based on individual system demands and paper grade quality requirements.

Some mills invest in packaged systems to provide high-pressure, high-temperature water systems to accelerate cleaning activities. These systems can provide a continuous flow of water/chemical combinations, at sufficient volume that provide complete coverage across the width of the machine, offering a distinct improvement over standard systems that have a single nozzle traversing the machine width.

A 2003 innovation by Nalco Water improved press section performance at several mills using a structured polymer solution sprayed onto the sheet. The result was increased water removal efficiency, which could either be seen by the mill as an opportunity to produce more tons (tonnes), or to produce constant tons (tonnes) at a reduced steam flow requirement, with increased sheet strength. Increased sheet dryness values of up to 8% leaving the press section have been observed with this program, resulting in energy savings of \$7/ton (\$7.7/tonne) of paper produced at an energy cost of \$8/million Btu (\$7.6/GJ).

Paper Machine Dryer Section

While the dryer section is only tasked with removing the remaining 4% of water that leaves the headbox, it is the most expensive section to operate. Drying occurs through water evaporation from the sheet as it passes over a series of steam heated cast iron drums (Fig. 32.18).

Most paper grades require sheet support as it progresses through the dryer section, which is provided by dryer felts. Heavier paper grades, such as linerboard, do not require such protection.

An important consideration on the sheet side outside of the dryer cans is the movement of water vapor away from the sheet once it has evaporated. Steam is the heating medium for the air, which comes in from outside the paper machine building across a series of coils. Many machines, especially modern wide ones need to blow air into the inner areas of the dryer section, so that the moist humid air moves away and the sheet dries uniformly. Since the space in between

Figure 32.18 Steam heated dryers evaporating the remaining water.

sequential dryer can cylinders is referred to as the pocket, these are called pocket ventilation systems.

Adding steam into and extracting condensate from the spinning dryer cans is a considerable engineering challenge. This is done through a device mounted onto the dryer can called a steam joint. The steam inlet is simply that of exhausting the vapor into the can interior. Condensate removal is accomplished through a shoe-like fitting that rotates around with the dryer as it spins. Centrifugal force forces the liquid condensate to the dryer can outer wall, and a pressure drop control system allows condensate to be efficiently extracted. Some steam, called blow-through steam, is allowed to exit the dryer can with the liquid condensate as a way of maximizing condensate removal. The condensate/blow-through steam combination is routed into a steam separator tank, with the flow from several dryer cans being combined. The steam is collected from the top of the separator and used as feed for either that same group of dryer cans, or dryer cans located toward the wet end of the machine.

The condensate dryer drainage system design has a major impact on the possibility of corrosion occurring. Older machines, those built prior to 1970, almost always had a cascade design as shown in Fig. 32.19 where the steam collected in a separator tank is routed toward the wet end, since wet end dryers operate at a lower steam pressure so as not to apply too much heat to the sheet too quickly. With this design, it was common to see an increased corrosion rate in the eventual condensate stream, since the flashing of carbon dioxide (CO_2) along with the steam served to depress the local condensate pH, to the point where it would be acidic and dissolve the steel materials of construction. Amine treatment selection for cascading systems relied heavily on cyclohexylamine, which being the most

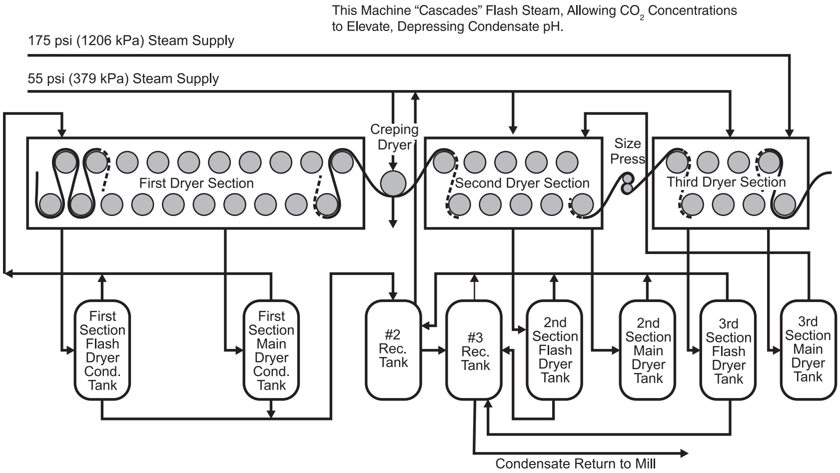

This Machine “Cascades” Flash Steam, Allowing CO_2 Concentrations to Elevate, Depressing Condensate pH.

FIGURE 32.19 Cascade design paper machine condensate drainage system.

volatile of the amines routinely used as condensate treatments, could best follow the CO_2 and neutralize any acid being created.

There is a condenser present at the wet end of the paper machine, where there are no lower-pressure sections to flash the steam. It condenses the steam phase into liquid condensate that can be added to the other condensate streams and pumped back to the powerhouse for reuse as boiler feedwater. These condensers typically use mill water on the shell side, and in the case of a tube leak, allow mill water to get into the purer condensate flow. A good monitoring program includes testing for hardness components and dissolved oxygen, both of which are present in mill water but not condensate. If a tube leak is found, a decision must be made to either discard the condensate, losing its thermal and water savings value, or accept the presence of the contaminants until the condenser can be repaired.

Modern paper machines feature a design that returns the steam collected in the outlet separator tanks back into the same dryer section, after having boosted its pressure via the use of a thermocompressor. The thermocompressor uses higher-pressure steam to educt the lower-pressure flash steam up to the steam pressure required for that dryer section. Because of this recycling of steam, the thermocompressor design can accumulate noncondensable gasses, and needs to be vented periodically to perform optimally. Modern paper machines tend to use the thermocompressor design as shown in Fig. 32.20, because of the ability to achieve better temperature control of the individual dryer sections. Amine treatment for a thermocompressor system is quite different than for the cascading design, since there is no mechanism to concentrate CO_2.

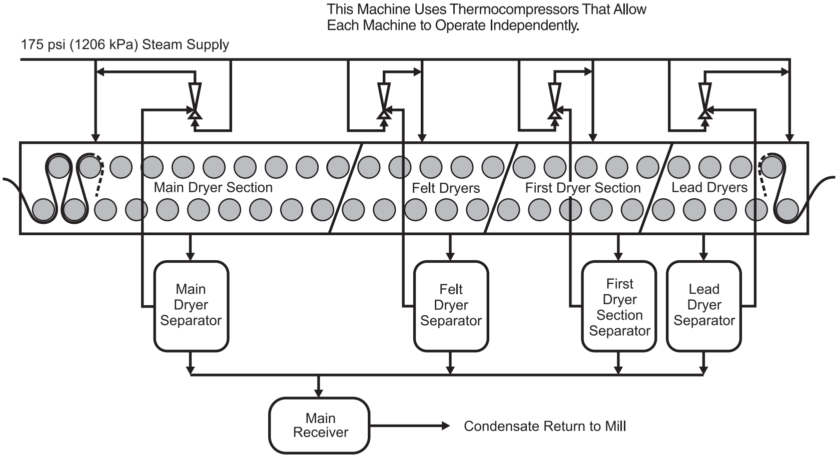


Figure 32.20 Thermocompressor design paper machine condensate drainage system.

Sophisticated computer controls using online sensors, control the speed at which the paper passes along the paper machine. When the targeted moisture content is achieved, the paper is taken on long rollers called reels. Samples are collected for quality control analysis, and the paper is ready to be converted into commercially sized rolls for delivery to the customer. Some paper machines apply a coating to the paper directly on the machine, usually as a liquid slurry or solution. This requires another dryer section in order to dry the sheet to its desired moisture content. Alternatively, the produced rolls of paper can be taken elsewhere for the application of a coating. There are no water treatment related applications or concerns in the converting process. Scrap paper, from either the direct production process or product not meeting targeted specification, is called broke, which is repulped and reused, much in the same way of recycled paper. This minimizes waste generated from the process.

Because their properties are so different, tissue and towel paper grades are produced on a different design of paper machine. The core of the tissue production process is a device called the Yankee dryer, which like the normal paper machine uses steam as the drying medium. Instead of using a series of dryer cans, the thinner sheet of tissue can be dried on a single dryer drum. This prevents excessive compaction of the tissue, which would reduce its tactile properties that consumers appreciate. The internals of the Yankee dryer are considerably different from the standard paper machine and can present a treatment challenge. Instead of a single pick-up shoe or siphon, the Yankee dryer internal design features a series of channels into which the condensed steam flows (Figs. 32.21 and 32.22). The term "soda straw" is often used to describe the small diameter tube

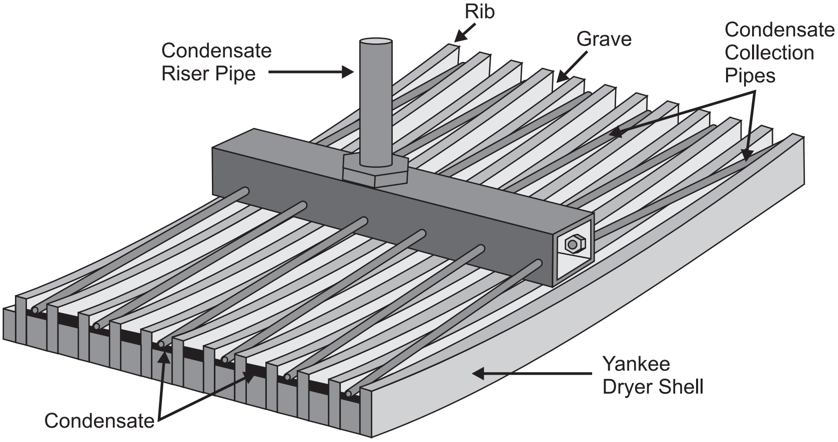


Figure 32.21 Yankee dryer condensate removal design.

inside each channel. Condensate flows through the many soda straws into a condensate collection system, and leaves the Yankee dryer, going into a tank called the First Separator. As in the standard paper machine, blow-through steam comes along with the condensate to minimize pressure drop. The flash steam leaves the First Separator and goes through a thermocompressor to be pressurized to the requirement of the Yankee dryer steam supply. This tight recycling arrangement can cause high concentrations of CO_2 to be present, making amine treatment of tissue mill systems expensive if there is no alkalinity removal in the boiler makeup water pretreatment system.

Figure 32.22 Yankee dryer. (*Courtesy of AER Corporation.*)

In some designs, the soda straws inside the Yankee dryer are formed of copper alloys that, unlike steel, undergo corrosion under both alkaline and acidic pH conditions. This makes Yankee dryer condensate pH control an important aspect of the treatment, since corrosion products generated can plug the small openings in the soda straws and limit production.

The sheet finishing, paper storage and warehousing, and loading dock areas of the paper mill have minimal water usage or water treatment needs. The exception is those mills in colder climates that require building heating. Heating systems often generate condensate that is collected and returned to the boilers for reuse as feedwater. Because these systems go off and on seasonally, and sometimes the same day, it is very likely that metal oxides will contaminate the condensate. Even though this would be a small fraction of the total condensate flow going to the powerhouse, the elevated potential for high concentrations of metal oxide contaminants warrants selection of either an advanced treatment program, mechanical filtration of the condensate, or an operational strategy to discard the condensate flow when it is most contaminated.

CHAPTER 33

The Power Industry

Steam-electric power generating plants are the largest industrial users of water in the world. As an example, the United States Geological Survey (USGS) found that in 2000, the electric utility industry withdrew 195 billion gallons of water per day (738 million m^3/d), accounting for 48% of total water withdrawals for all uses in the United States. Approximately, one-third of the total was saline, and two-thirds was freshwater.

The laws of thermodynamics limit the amount of the energy in fuel that can be converted to work by a steam turbine. More than 50% of the initially available heat remains in the exhaust steam leaving the turbine, and most of this is rejected to cooling water and then lost to the surrounding environment. Cooling water required for condensing the turbine exhaust steam in a 1000 MW plant is about 576 mgd (1500 m^3/min).

By comparison, other water requirements for steam-electric plants are small. These include replacement of losses from the steam cycle, ash transport (in coal fired plants), flue gas cleaning, equipment cleaning, and domestic uses. Once-through cooling water is used in many power plants and is returned directly to its source. Because the condenser outlet water is typically 5 to 25°F (3–14°C) warmer than the inlet, heat is a principal concern in the discharge of once-through cooling water. In many countries, the elimination of this thermal discharge, which can affect aquatic species downstream, is an environmental goal.

The difference between total water withdrawal and final discharge is primarily lost to evaporation, which occurs principally from ponds and cooling towers used in recirculating cooling water systems. There is also some water loss from the surfaces of ash settling ponds. Minor water losses can occur by seepage into the ground from unlined ponds and in wet ash or water treatment sludge hauled from the plant.

This chapter is primarily concerned with high-pressure (HP) boilers operating above 1000 psig (6.9 MPag). These boilers typically use high-purity feedwater and have high heat flux, both of which demand specialized internal boiler water treatment and careful control. Some low-pressure (LP) boilers also use high-purity feedwater and require the types of treatment programs discussed in this chapter. Chapter 11 on Boiler Feedwater Treatment discusses common internal treatment programs for lower-pressure boilers. Most often, operators of high pressure electric utility boilers take guidance from the Electric Power Research Institute (EPRI), VGB Powertech or other organizations such as the International Association for the Properties of Water and Steam (IAPWS), when selecting a treatment program and chemistry limits for the water-steam cycle.

Energy Conversion

In steam-electric power production, the chemical energy of fossil fuels or the nuclear energy of fissionable materials is converted to heat for the generation of steam, which is then converted to mechanical energy in a turbine coupled to an electric generator. Exhaust steam is condensed and returned to the boiler.

The theoretical efficiency at which heat in the steam can be converted in a turbine to work within the fluid (water-steam) cycle of a steam-electric plant is shown by Eq. (33.1):

$$\text{Percent theoretical efficiency} = 100(T_1 - T_2)/T_1 \tag{33.1}$$

where T_1 = absolute temperature of the turbine inlet steam, R (K)
T_2 = absolute temperature of the turbine exhaust steam, R (K)

Thus, the greatest efficiency is achieved by providing the highest inlet steam temperature T_1 and lowest exhaust temperature T_2 practical for a given turbine-condenser system.

In practice, upper temperatures are limited by the strength of metals available for boiler and superheater construction. Strength falls off rapidly as temperature exceeds 900°F (482°C, 1360 R, 755 K). Upper temperatures are generally limited to a maximum of about 1100°F (593°C, 1560 R, 866 K). A significant temperature difference is required to cause heat to flow from the exhaust steam to the cooling medium circulated through the condenser. The practical effect is that lower steam temperatures on condensing turbines typically range from 80 to 120°F (27–49°C, 540–580 R, 300–322 K), even with cooling water at 40°F (4.4°C) in the winter. Within these upper and lower temperatures, then, the best theoretical efficiency would be:

$$\text{U.S. Units: Theoretical Efficiency} = 100(1560 - 540)/1560 = 65.4\%$$

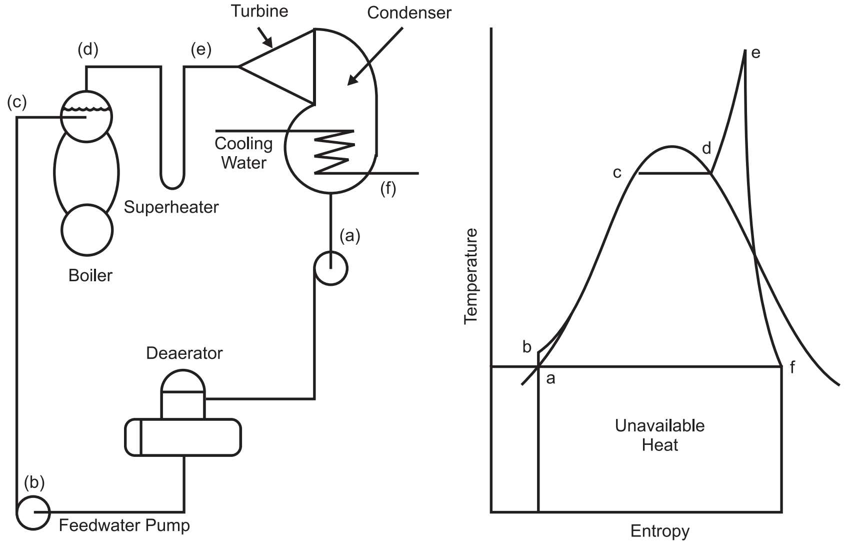
$$\text{Metric Units: Theoretical Efficiency} = 100(866 - 300)/866 = 65.4\%$$

Achievable efficiencies are considerably lower than theoretical, both for the fluid cycle and for the generating plant as a whole. Significant energy is lost in overcoming fluid and mechanical friction. Sizable amounts of energy are consumed in the operation of the plant's feedwater pumps, boiler draft fans, and other auxiliaries. A power plant's pollution control equipment, required to meet air emission and water discharge standards, can consume as much as 10% of the electrical output. Actual steam-electric plant overall efficiencies range from 35 to 45% for conventional units and 55 to 60% for modern combined cycle systems.

The Power Cycle

The energy flow through the water-steam phase changes in a steam-electric plant is called the Rankine cycle. The Rankine cycle has four basic stages: boiler, turbine, condenser, and feedwater pump.

The Rankine cycle may be illustrated by several kinds of diagrams. Figure 33.1 shows that cycle relating the change in temperature of the fluid to its entropy at each stage in the cycle. Entropy is a measure of that portion of the heat received by a cycle that cannot be



a to b: Liquid Heating and Compression (feedwater pump).
b to e: Reversible Heat Addition in Feedwater Heaters (b to c), Boiler (c to d), and Superheater (d to e).
e to f: Steam Expansion and Conversion of Heat Energy to Work.
f to a: Reversible Rejection of Unavailable Heat to Cooling Water.

FIGURE 33.1 Steps in the Rankine cycle from the introduction of water as a liquid into the system, through its phase change to steam that produces work in a turbine, to the condensing of the exhaust vapor to water again for return to the boiler.

converted into work, because of the random motion of gas (steam) molecules. Entropy is expressed mathematically as the ratio of heat content to temperature.

To achieve the highest possible thermodynamic efficiency, modern fossil-fuel power cycles use steam superheaters and reheaters to raise the average temperatures (T_1) of steam flowing through the turbine. Condensers operating under vacuum permit expansion of steam to the lowest possible exhaust temperature (T_2). To further recover as much heat as possible, partially expanded steam is extracted from the turbine at various points for heating feedwater (called "regenerative heating"). Figure 33.2 illustrates a cycle having these components, and Fig. 33.3 illustrates their effect on a temperature-entropy diagram of the cycle.

Nuclear steam-electric plants of the light water reactor types typical in commercial service, cannot deliver steam at the temperatures achieved in fossil-fuel units. Nuclear pressurized water reactors (PWRs) (Fig. 33.4) employing once-through steam generators achieve a relatively small degree of steam superheat [30–60°F (17–33°C)]. In PWR cycles, employing recirculating U-tube steam generators and in boiling water reactor (BWR) cycles (Fig. 33.5), there is no superheat.

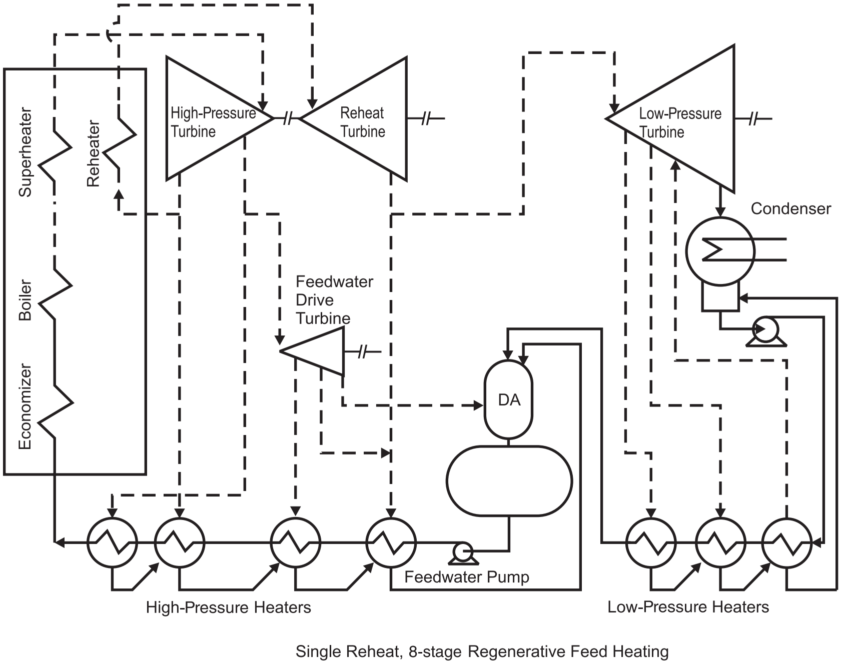


FIGURE 33.2 Addition of steam reheat and regenerative feedwater heating to increase cycle efficiency. Single reheat, 8-stage regenerative feedwater heating, 3515 psia/1000°F/1000°F steam (24.2 MPaa/538°C/538°C steam).

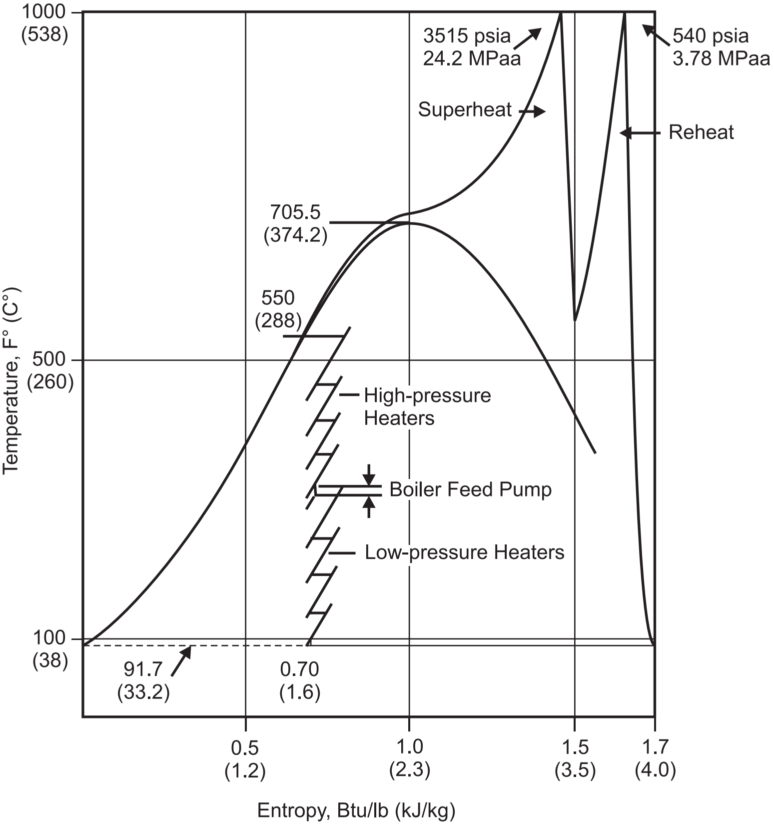


FIGURE 33.3 Modified Rankine cycle showing the effect of reheating steam and adding feedwater heaters to the cycle. (*Adapted from Steam—Its Generation and Use, Babcock and Wilcox Company, 1972.*)

For this reason, nuclear power cycles are limited to efficiencies of about 32% compared to 36 to 39% for fossil-fuel cycles, since less heat is supplied to the turbine (T_1).

In fossil-fuel units, further improvements in thermodynamic efficiency are achieved by economizers and air preheaters installed in the flue gas path between the boiler and stack. Economizers transfer heat from the flue gases to the feedwater. Air preheaters transfer some of the remaining flue gas heat to the boiler's combustion air supply.

For still higher efficiencies, where suitable fuels are available, combined cycle steam-electric plants combine the operation of a combustion turbine with that of a steam turbine. In combined cycle generating plants (Fig. 33.6), the hot combustion turbine exhaust gasses are used in a heat recovery steam generator (HRSG) to produce steam to drive a steam turbine.

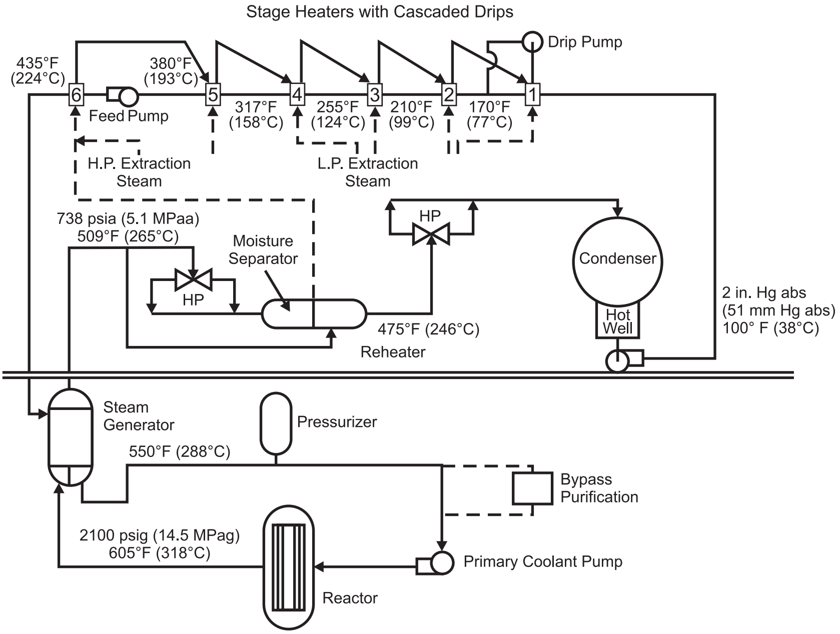


Figure 33.4 PWR nuclear power cycle showing major components and typical pressures and temperatures. (*Adapted from The Effects of Water Quality on the Performance of Modern Power Plants, Klein and Goldstein, NACE 1968 Conference*.)

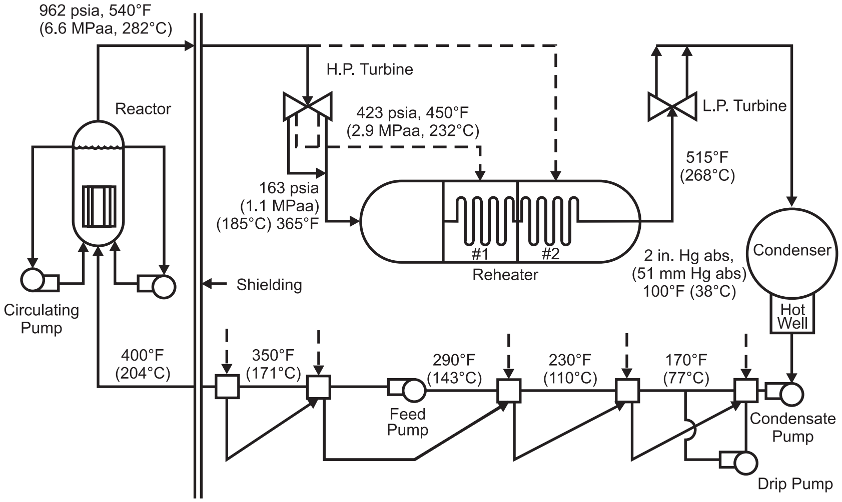


Figure 33.5 BWR nuclear power cycle showing major components and typical pressures and temperatures. (*Adapted from The Effects of Water Quality on the Performance of Modern Power Plants, Klein and Goldstein, NACE 1968 Conference*.)

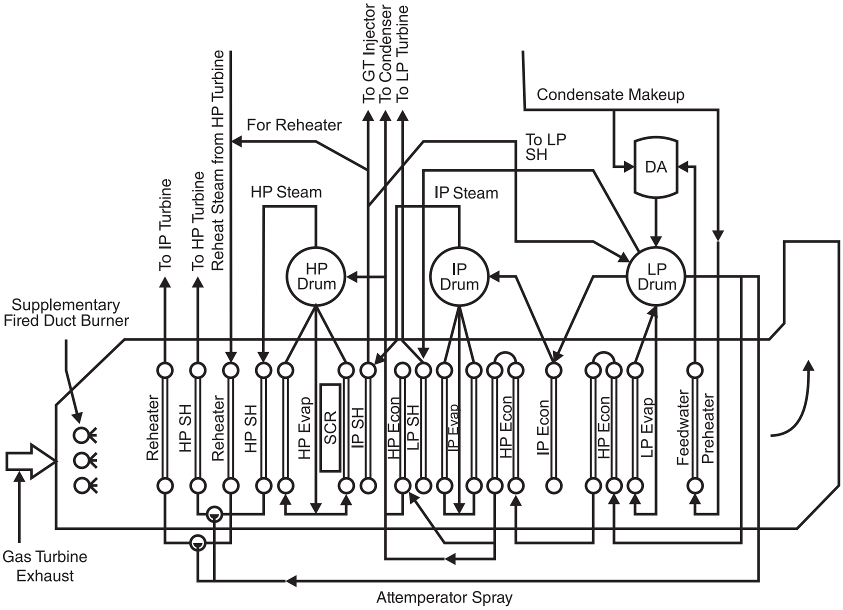


Figure 33.6 Combined cycle unit triple drum HRSG.

Water: The Working Fluid

In steam-electric power cycles, water is subjected to wide variations in temperature and pressure in the cyclic sequences of compression, heating, expansion, and heat rejection. Temperatures may range from 70 to 1200°F (21–650°C) with pressures from 0.5 to 5000 psia (3.4 kPaa to 34 MPaa).

As shown by the diagram in Fig. 33.7, steam density approaches that of water as pressure increases, until the critical pressure is reached at 3200 psia (22 MPaa). A supercritical fluid exists above this pressure, which cannot be considered either steam or water. Boilers operating over 3200 psia (22 MPaa) are called supercritical units.

In cycles operating at pressures below critical pressure, where steam density is less than that of water, phase changes occur from water to steam, and then from steam back to water. While there are advantages favoring drum-type boilers (Fig. 33.8) for most subcritical pressure cycles, once-through boilers are sometimes used because of lower initial costs.

Drum-type boilers have advantages in subcritical steam generation. They can produce high-purity steam with less stringent feedwater purity requirements, especially when the operating pressure is

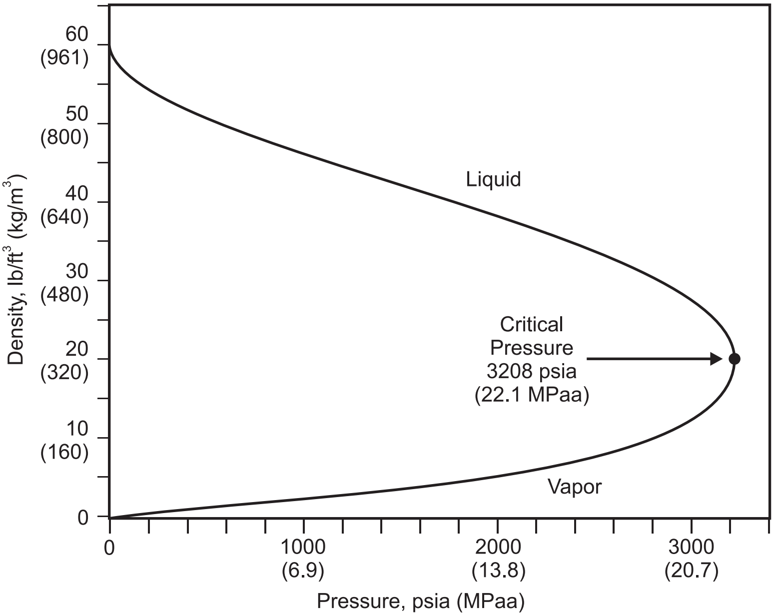


Figure 33.7 As boiler pressure increases, steam density and water density, which are greatly different at atmospheric pressure, approach each other, becoming equal at 3200 psia (22 MPaa), the critical pressure.

less than 2500 psig (17.2 MPag). Mechanical separation of steam from the recirculating boiler water leaves most of the undesirable solids behind in the boiler. Because boiler internal recirculation rates are about four times the rate of steam flow from the boiler, the fluid rising to the steam drum from the generating tubes will be about 75% water.

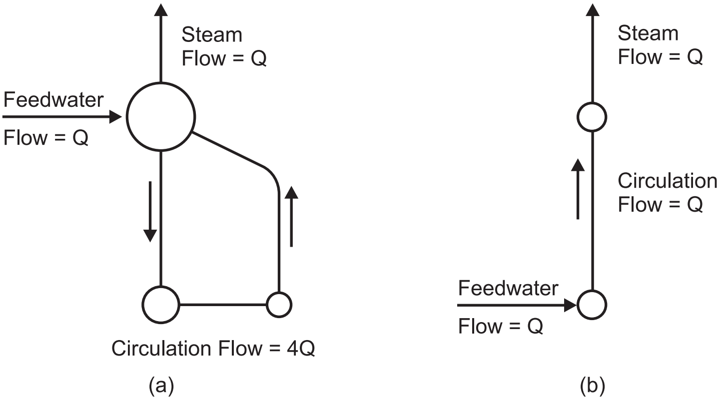


Figure 33.8 The basic differences between (a) drum-type and (b) once-through boilers.

This means that superheated steam, in which some boiler water impurities would become soluble, cannot exist in the boiler drum. Additionally, drum-type boilers are "simpler" to operate than once-through boilers.

In subcritical once-through boilers, a complete phase change occurs, with water entering at one end and superheated steam leaving at the other. There is no recirculation within the unit, nor is there a drum for mechanical steam-water separation. Boiler blowdown is impossible, so to prevent deposition of solids in the system beyond the point of water-steam phase change, requires stringent feedwater purity requirements, considerably higher than for drum-type boilers. In addition, that point of phase change must be located in a very low heat flux area of the boiler.

For cycles operating above critical pressure, no phase change occurs, so no steam-water separation is possible. Thus, at supercritical pressures, all steam generators are once-through.

In higher subcritical pressure cycles [2750–2850 psia (19.0–19.7 MPaa)], the margin of difference between the feedwater purity requirements of drum and once-through boilers is reduced. At such pressures, the effective mechanical steam-water separation is an advantage provided by drum-type boilers, but the advantage is limited by the increased difficulty in separating water from steam, as the densities of steam and water approach each other (Fig. 33.7). Also, mechanical separation devices in a boiler drum cannot remove the solids dissolved in the steam (vaporous carry over). For HP utility boilers, therefore, the concentration of solids in the steam is determined to an important extent, by their steam-water solubility ratios at the operating pressure. Silica is a well-known example of a compound that has increasing steam solubility with increasing pressure (Fig. 33.9).

If solids concentrations in the steam were to average 30 μg/L, for example, a 200 MW turbine would receive more than 200 lb/y (91 kg/y) of potential depositing solids. The portion that would deposit in the turbine and the portion that would remain in the steam to recycle with the condensate to the boiler cannot be accurately predicted. However, to avoid excessive turbine fouling, experience has shown the necessity of keeping total salt concentrations in the steam below 20 μg/L with silica not to exceed 10 μg/L. Further, to minimize any potential for stress corrosion cracking of turbine members, the steam solids should be free of sodium hydroxide and sodium chloride. While silica is potential foulant in the steam turbine, sodium hydroxide, sodium chloride, and sodium sulfate are potential corrodents (see Table 33.1).

Water purity is important for a different reason in nuclear power cycles. Although water becomes only slightly radioactive under neutron flux, producing only short-lived isotopes, the response of materials in the water under flux is of concern. Naturally occurring

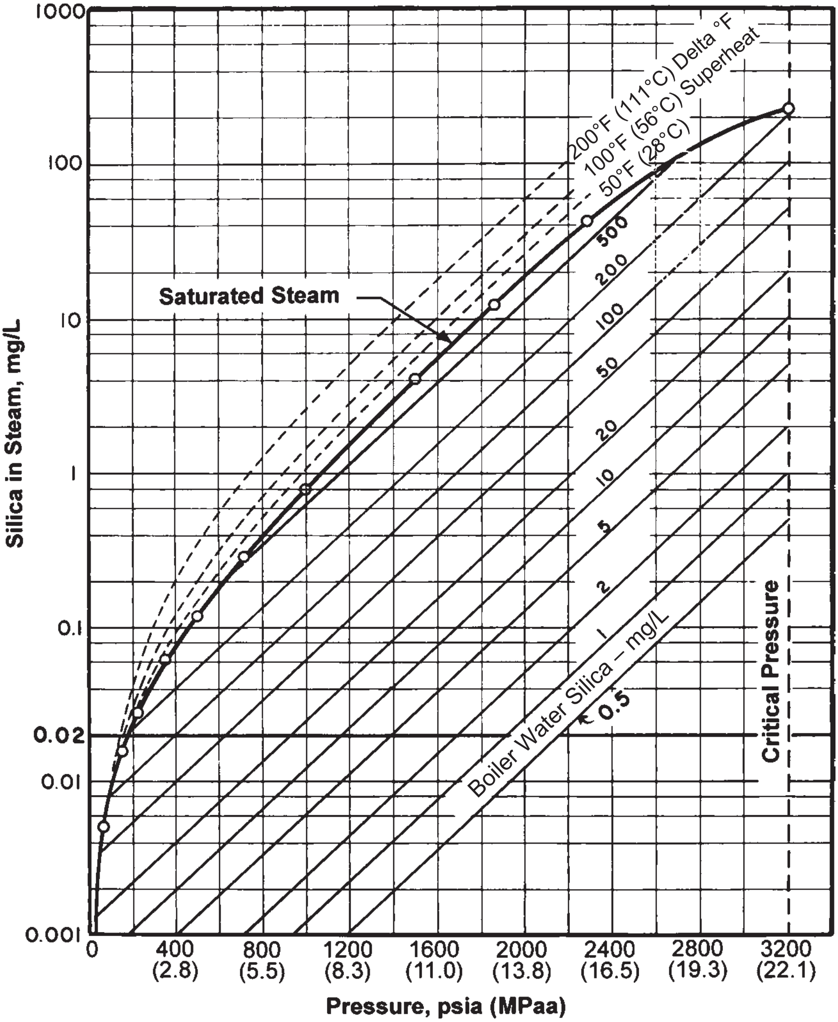


Figure 33.9 Distribution of silica between boiler water and steam.

cobalt, for example, would be an extremely undesirable constituent of primary coolant water passing through the reactor core in either BWR or PWR cycles. The product would be highly radioactive, emitting high-energy gamma rays during subsequent decay. Therefore, cobalt must be avoided in such systems. Since most other metals also produce radioactive isotopes under neutron flux, the tolerance for feedwater and steam cycle corrosion products is limited in nuclear cycles for operating and maintenance safety.

Although the required degree of purity varies for different cycles, relatively high-purity water is required for all modern power cycles.

Location	Parameter	Unit	Treatment Program			
			OT	AVT	PT	CT
Makeup	Specific Conductivity	μS/cm	≤0.1	<0.1	<0.1	<0.1
Makeup	Na, Cl, SO_4	μg/L	≤2	<2	<2	<2
Makeup	Silica (SiO_2)	μg/L	≤10	<10	<10	<10
Makeup	TOC	μg/L	≤100	<100	<100	<100
Feedwater	Cation Conductivity	μS/cm	≤0.15	0.2	0.2	0.2
Steam		μS/cm	≤0.15	0.2	0.2	0.2
Steam	Na, Cl, SO_4	μg/L	≤2	2	2	2

AVT, all-volatile treatment (oxidizing or reducing); CT, caustic treatment; Na, Cl, SO_4, sodium, chloride, and sulfate; OT, oxygenated treatment; PT, phosphate treatment; TOC, total organic carbon.

Source: EPRI Comprehensive Cycle Chemistry Guidelines for Fossil Plants, 2011.

Table 33.1 Feedwater and Steam Purity Specifications

Many water constituents must be measured and controlled at parts per billion (ppb or μg/L) concentration levels, compared to their measurement and control at parts per million (ppm or mg/L) concentrations in lower-pressure cycles or nonutility boilers.

Makeup water of the purity required for utility steam cycles can be produced reliably and at reasonable cost, by combinations of pretreatment equipment including reverse osmosis (RO), ion exchange, electro deionization (EDI), evaporation, and other pretreatment methods. Because makeup water volumes are usually 1% or less of total feedwater in typical power cycles, the major problem has become keeping the water pure after it has entered the cycle.

The two main sources for contamination of high-purity water are corrosion and inleakage. Corrosion represents not only metal damage, but also contamination of the system water with corrosion products that may then deposit in the boiler or turbine. Low-purity cooling water may enter the steam cycle at points of high vacuum (the surface condenser), and this inleakage is a second major source of contamination. Careful design and selection of materials of construction minimize the occurrence of these problems.

Factors Affecting Chemical Treatment

HP boiler systems operate at pressures of 1000 psig (6.9 MPag) or greater. Several factors, including higher boiler water temperatures and longer boiler water holding times will dictate the choice of chemical treatment program.

Several factors must be taken into consideration when treating water in HP boilers. The most significant factors are discussed here.

Higher boiler water temperature, which increases as operating pressure increases, has significant impact on water treatment programs. At 500 psia (3.4 MPaa), for example, the saturation temperature of boiler water and boiler water-steam mixtures is 467°F (242°C). At 1800 psia (12.4 MPaa), saturation temperature is 621°F (327°C). Fireside-waterside temperature differentials are thus reduced, and as a result, boiler tube metal temperatures are higher. Tolerance for waterside deposits, which further elevate tube metal temperatures, is therefore significantly reduced. At the same time, HP boiler water temperatures often exceed permissible maximum temperatures for organic polymer chemicals that might otherwise be useful for deposit control.

Longer boiler water holding time, especially when coupled with higher boiler water temperatures, further restricts the use of thermally degradable organic treatment chemicals. With expensive high-purity feedwater, HP boilers often operate at 50 to 100 cycles of concentration (COC) (2–1% blowdown). Some utilities operate up to 200 cycles or 0.5% blowdown. This means very long residence times for each molecule of water and chemical in the boiler. Even where boiler water temperatures do not actually exceed upper limits for some treatment chemicals, holding times may need to be reduced by increasing boiler blowdown to 2% or more to achieve good results. Blowdown capability may be limited by the amount of makeup water available.

Smaller density differences between water and steam, at elevated pressures, reduce the natural tendencies of steam and water to separate from each other in a boiler steam drum. In a boiler operating at 500 psia (3.4 MPaa), for example, water is 47 times heavier than steam, but in an 1800 psia (12.4 MPaa) boiler, water is only 8.8 times heavier. Feedwater purity and proper control of boiler water concentrations, as well as the mechanical efficiency of steam separator and dryer equipment in the boiler drum, become extremely important as a result.

High saturated steam temperatures in the boiler drum significantly affect the solubility and selective carryover of certain boiler water constituents in the steam. This is particularly true of silica above 600 psia (4.1 MPaa) and to a lesser extent, sodium above 2400 psia (16.5 MPaa). As drum steam pressure and temperature increase, concentrations of silica and sodium in the steam increase with respect to the silica and sodium remaining in the boiler water.

Terminology

A familiarity with the following terms helps promote an understanding of HP boiler systems.

High-pressure boiler systems—From the standpoint of water treatment requirements, boilers in which steam is produced at or above 1000 psia (6.9 MPaa).

Units of measure—Boiler pressure is most commonly expressed in terms of pounds per square inch (psi) in U.S. units and kilopascals (kPa) or megapascals (MPa) in SI units. Readings provided by standard pressure gauges on boilers and control panels, which are only of pressures above atmospheric, are correctly expressed as psig in U.S. units and kPag or MPag in SI units. For a given gauge pressure reading, the total pressure, including atmospheric is expressed as pounds per square inch absolute (psia) in U.S. units or kPaa or MPaa in SI units. The properties of water and steam shown in engineering steam tables always express pressure in psia in U.S. units and kPaa or MPaa in SI units. Gauge readings may be converted to absolute pressure simply by adding atmospheric pressure (approximately 14.7 psi or 101 kPa at sea level) to the gauge readings.

$$1 \text{ psi} = 6.89 \text{ kPa or } 0.00689 \text{ MPa}$$

Utilities commonly use the term "cycle pressure" to describe a unit's turbine throttle pressure, for example, 1800 psi (12.4 MPa) or 2400 psi (16.5 MPa). Steam drum pressure is normally 150 to 250 psi (1–1.7 MPa) higher than the throttle pressure. This loss is caused by pressure drop across the superheaters and connective piping.

Subcritical-pressure boilers—Those boilers that operate below the critical pressure of 3200.2 psia (22.1 MPaa), at which steam and water densities become equal.

Supercritical-pressure steam generators—Frequently encountered in some large electric utility stations, they produce steam at or above the critical pressure. Since there is no density difference by which steam and water can be separated in a boiler drum, supercritical steam generators are necessarily once-through types. Such units may be compared to a continuous length of heated pipe. The feedwater enters at one end and supercritical-pressure steam leaves the other for subsequent superheating in a conventional superheater arrangement.

Most supercritical electric utility units operate at a nominal 3800 psig (26.2 MPag) and have a turbine throttle inlet pressure of 3500 psig (24.1 MPag). Currently, the highest design pressure for a unit is about 5000 psig (34.5 MPag), and this unit actually operates at about 4500 psig (31 MPag).

Water Chemistry in Fossil-Fuel Plants—Liquid Phase

Apart from steam purity considerations, a major goal of cycle water chemistry and treatment control is the prevention of tube metal failures in HP steam generators.

Because makeup water is demineralized and essentially free of measurable hardness and other solids, tube failure due to waterside scale and deposits is far less likely to occur in utility plants, than in lower-pressure industrial boilers. Instead, in power plant drum-type boilers, tube metal failures are more commonly due to highly localized "crater" or "ductile gouging" forms of waterside corrosion, waterside hydrogen penetration and embrittlement of carbon steel, and corrosion fatigue.

The ductile gouging form of corrosion is a chemical attack characterized by irregular craters in the tube wall. The tube fails when wall thickness at the point of wastage is insufficient to withstand the internal pressure. The most common chemical agents in this form of attack are sodium hydroxide and phosphate. Even with a bulk boiler water within acceptable levels of contaminants as determined by usual methods of testing, a porous deposit on the tube wall provides a mechanism for concentrating chemical in contact with the tube surface, to several thousand milligrams per liter. Sodium hydroxide and phosphate concentrate in this manner and react first with the magnetite tube surface, and then with the elemental iron of the tube to form soluble iron complexes. For example, in the case of sodium hydroxide:

$$4\mathrm{NaOH} + \mathrm{Fe_3O_4} \rightarrow 2\mathrm{NaFeO_2} + \mathrm{Na_2FeO_2} + 2\mathrm{H_2O} \tag{33.2}$$

$$\mathrm{Fe} + \mathrm{NaOH} + \mathrm{H_2O} \rightarrow \mathrm{NaFeO_2} + 3\mathrm{H} \tag{33.3}$$

The parent tube metal is thus exposed to react with water to reform protective magnetite.

$$3\mathrm{Fe} + 4\mathrm{H_2O} \rightarrow \mathrm{Fe_3O_4} + 8\mathrm{H} \tag{33.4}$$

In either case, localized wastage of tube metal occurs and hydrogen is produced as a reaction product. The atomic hydrogen thus produced is capable of intergranular penetration of steel and of reaction with carbon in the steel to form methane gas.

$$4\mathrm{H} + \mathrm{C} \rightarrow \mathrm{CH_4} \tag{33.5}$$

Not only is the steel thus weakened by decarburization along its grain boundaries, but the formation of methane develops pressure between grains in the steel microstructure, producing intergranular

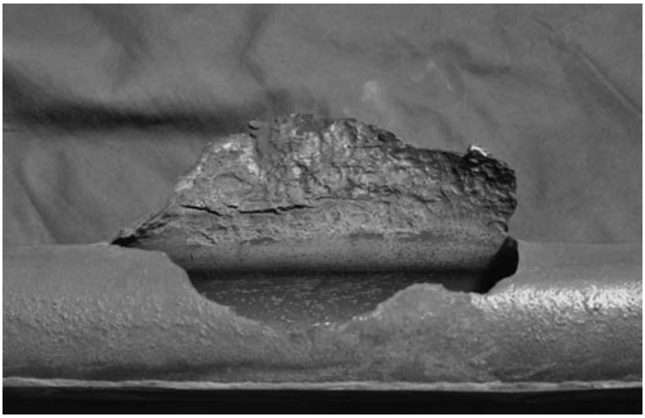


Figure 33.10 Example of hydrogen damage resulting in a thick-edged failure window in a boiler tube.

cracks. The result is failure of the tube wall, when such intergranular decarburization and micro fissuring have sufficiently reduced its strength. Although some waterside wastage of metal may have occurred in the corrosion reaction that produced the hydrogen, hydrogen damage normally results in thick-edged fracture before the wall thickness is reduced to the point that stress rupture occurs. In such thick-edged or "brittle" fracture failures, it is not uncommon for an entire irregularly shaped "window" to be blown out of an affected tube (Fig. 33.10).

In summary, the major causes of ductile gouging and hydrogen damage of carbon steel tubes are (1) a chemical agent that will be corrosive if sufficiently concentrated and (2) a concentration mechanism. For more information on boiler failure types and causes, refer to The Nalco Guide to Boiler Failure Analysis, 2nd edition

There are several mechanisms capable of producing high, localized salt concentrations. Any condition of heat input, in excess of the cooling capacity of the flow of fluid circulating through a tube can result in film boiling on the metal surface, with evaporative concentration of salts occurring. Localized pressure differentials, as created by high velocity through a tube restriction such as a welding back-up ring can result in small pockets of "flashing" water, concentrating salts on the downstream side of the restriction. The most common mechanism is preboiler corrosion, with pickup of metals and the subsequent deposition on heated boiler tube surfaces, where they function as porous deposits. Evaporation beneath the deposit draws in boiler water to replace evaporation loss, but prevents solids from leaving the area. This phenomenon is commonly called "wick boiling" and is shown in Fig. 33.11.

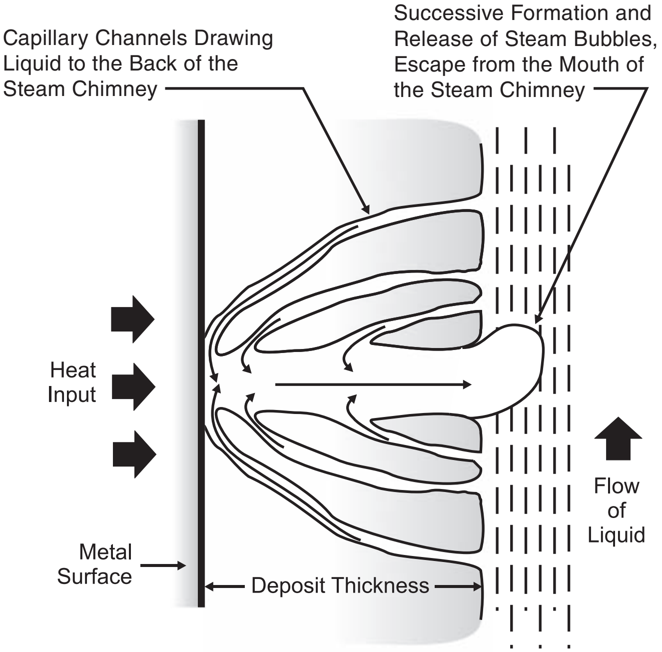


FIGURE 33.11 Wick boiling.

To prevent such corrosion and hydrogen damage, all concentration mechanisms must be eliminated, or potentially corrosive chemical agents must be excluded from the boiler water. Since porous deposits of preboiler corrosion products create the most common mechanism for chemical concentration, strict attention to protection of preboiler metal surfaces is critical, and periodic chemical cleaning to remove these deposits is required.

A significant characteristic of modern utility cycles is the high ratio of preboiler surface area to that in the boiler itself. While a ratio of about 0.3 would be typical in a 750 psia (5.2 MPaa) system, a ratio of about 1.3 would be typical at 2800 psia (19.3 MPaa). This is a reflection of the multiple stages of regenerative feedwater heating, commonly employed to increase cycle efficiency. To the water engineer, the higher ratio means that the area from which metals can be picked up is larger than the area on which they are likely to deposit.

Metals used in fabrication of condensers and feedwater heaters are commonly stainless steels and alloys of copper, such as brass, cupro-nickel, and monel. Thus, iron and copper are the principal contaminants likely to be acquired by feedwater en route to the steam generator.

Feedwater pH is an important factor in minimizing preboiler corrosion of metals. For iron and its alloys, feedwater pH values in the range of 9.2 to 9.6 are considered optimum. For copper and its alloys, feedwater pH values generally should be in the range of 9.0 to 9.3. Volatile alkalis such as ammonia and organic amines that will not contribute dissolved solids are commonly used for pH control in the condensate-feedwater portion of the steam cycle.

Feedwater oxygen also has a great bearing on preboiler corrosion and contamination. An oxygen level of 10 μg/L or less at the condensate pump discharge is usually specified. The largest potential for oxygen admission occurs in the high-vacuum portions of the cycle. Oxygen can be reduced to low levels mechanically, either in deaerating surface condensers or in separate deaerators located ahead of HP feedwater pumps. For removal of residual oxygen, reducing agents like hydrazine may be injected continuously immediately downstream of the condenser. Hydrazine is a chemical oxygen scavenger that introduces no solids to the cycle. Its concentration is controlled in the range of 10 to 20 μg/L in the feedwater, usually measured at the economizer inlet. Because of the potential risk to personnel handling hydrazine, a carcinogen, proprietary substitutes have been developed that react very much as hydrazine. The most widely used substitutes contain carbohydrazide or isoascorbic acid.

System metallurgy must also be considered when selecting feedwater and condensate treatment programs. The preboiler equipment in many plants contains both copper alloy and mild steel metallurgies. Current technology can optimize the passivation of each of these materials separately, but not for both materials in the same system. Copper oxide formation, for example, requires a strong reducing environment, while steel oxides become more passive under neutral or slightly oxidizing conditions. For example, dissolved oxygen (DO) levels of 2 to 4 μg/L provide the optimum environment for passivation of all-steel systems, but would cause corrosion of the copper alloys.

Many plants utilize online oxidation-reduction potential (ORP) analyzers to monitor the oxidizing environment in the condensate and feedwater. The same measurement can be used to control passivator/scavenger feed. Increasing DO increases the oxidizing potential (ORP) of the condensate and feedwater.

Based on EPRI studies conducted in 2000, maintenance of a reducing environment is essential in controlling copper corrosion in the condensate and feedwater cycles. Copper corrosion control is accomplished by converting cupric oxide (CuO) to cuprous oxide (Cu_2O), which forms a stable and more durable protective film. For copper-based systems, it is imperative that the condenser, feedwater heaters, and piping be maintained in a reducing state of at least –50 mV at all times, including standby conditions. The recommended limits for normal operation are –150 to –250 mV in the feedwater of mixed metallurgy systems. (These limits are extremely difficult to meet in cycling units and may require unit specific standby procedures to accomplish.)

Newer combined cycle HRSG and coal-fired units are constructed without the use of copper alloys in the steam cycle. In addition, many older coal-fired units replaced copper-alloy feedwater heater and condenser tubes, to remove the corrosion and deposition problems associated with copper alloys. That enables these units to focus specifically on minimizing steel corrosion. Fundamentally, oxide films formed on mild steel are more durable when formed at higher pH and with greater concentrations of oxygen. Durability increases as a result of plugging the voids and imperfections in the magnetite (Fe_3O_4) film with hematite (Fe_2O_3). This "plugging" action helps prevent impurities from reaching the base metal. Improved stability in the oxide film reduces both general corrosion and flow-accelerated corrosion (FAC), critical to reduction in corrosion product transport and chemical cleaning frequency requirements. Current guidelines recommend that the room temperature ORP in all-ferrous feedwater systems be controlled between ≥0 and +50 mV for all-steel systems. EPRI recommends that units with high-purity feedwater (<0.2 μS/cm cation conductivity) and low DO (<10 μg/L at the condensate pump discharge) eliminate the use of oxygen scavengers/passivators. Iron transport and soluble iron studies should be performed before and after eliminating the oxygen scavenger/passivator to confirm iron transport values are reduced, preferably below 5 μg/L. Feed of oxygen scavenger/passivator may provide a benefit, if the boiler feedwater purity degrades, if the unit changes to cycling duty, or if the unit is removed from service on a frequent basis. Iron transport and soluble iron studies are essential in evaluating the need for, and the impact of, oxygen scavenger/passivator feed.

Ammonia, an important variable in copper alloy corrosion, is generally present in power cycles, either due to direct addition or decomposition of chemicals such as hydrazine or amines that have been added to the system. In sufficient concentrations, ammonia reacts directly with copper to form soluble complexes, or it can contribute to stress corrosion cracking of copper alloy tubes. Even at lower concentrations, ammonia can react with protective copper oxides on condenser and heater tube surfaces, exposing parent metal to wastage by reaction with oxygen in the feedwater. To minimize copper corrosion, many operators limit the maximum cycle ammonia concentration to 0.3 to 0.5 mg/L. The ammonia limits can be met, by carefully controlling chemical additions to the cycle, and by proper regeneration of condensate polishers. If the ammonia concentration increases beyond the desired maximum, temporarily dumping the normally recycled air removal system's after-cooler drains (Fig. 33.12) will help remove the excess from the system.

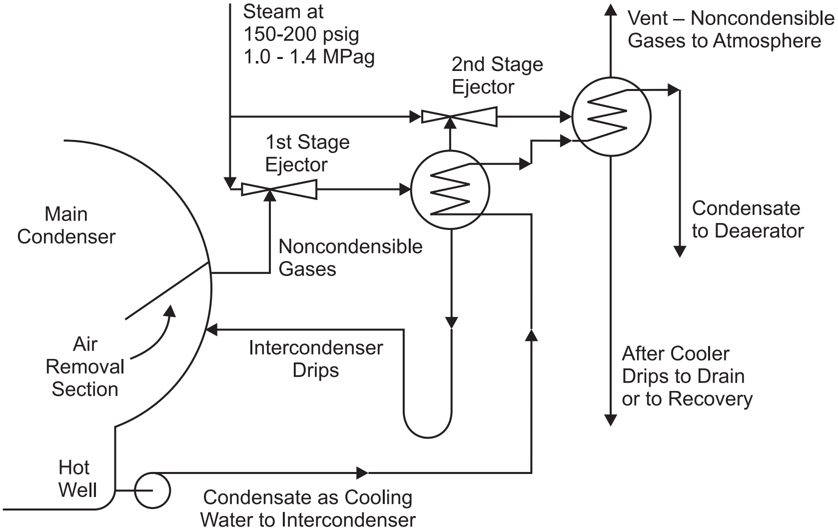


FIGURE 33.12 Noncondensable gases, including air from inleakage and ammonia from the steam cycle, are removed by ejection and inter and after-condensers. Final drips may be reclaimed or discarded, if concentrations are too high.

Good design calls for careful selection of materials of construction to withstand the environment of the preboiler system. Condenser tubes in freshwater coolant service are commonly brass, cupro-nickel, stainless steel, or titanium. LP stage heaters commonly use brass, cupro-nickel, or stainless steel alloys, except for supercritical pressure cycles, where even minute concentrations of copper can cause serious turbine fouling problems and the use of steel alloys is required. HP stage heaters are fabricated of cupro-nickel alloys, stainless steel, and carbon steel.

It is common practice to reduce metallic "crud" in utility feedwater by polishing the condensate through a filter of mixed cation and anion exchange resins. Filtration removes the insoluble crud, and ion exchange removes any dissolved contaminants that have entered the cycle by inleakage.

As shown in Fig. 33.13, polishers are generally located between the condenser and the first feedwater stage heater. This is due to the fact that a large part of the vulnerable preboiler metal surface area is in the condenser and on the steam side of stage heaters, cascading heater condensate drips back to the condenser. This placement protects high-temperature feedwater heaters, the steam generator, and the turbine from deposit-forming contaminants. Temperature limitations on ion exchange resin control the location of polishers in the cycle. Regenerable polishers can withstand only about 120°F (50°C) and must be confined to the condenser outlet. Powdered resin units

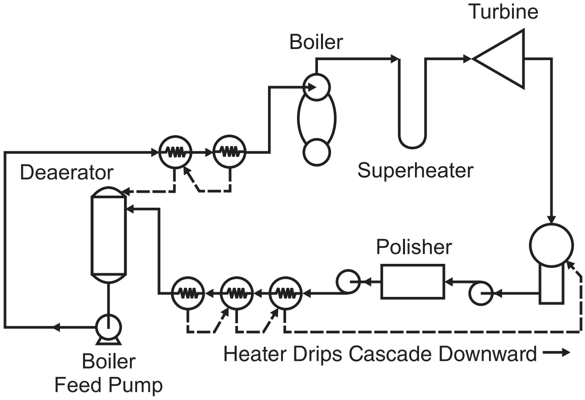


Figure 33.13 Power cycle with full-flow condensate polishing.

may be placed in higher-temperature locations, but still in the lower-pressure stage heater train.

For the best cost performance, regenerable mixed bed polishers are commonly operated at service flow rates over 50 gpm/ft^2 (122 m^3/[h · m^2]), about 10 times the rate employed in raw water demineralization. In some cases, to avoid any possibility of contaminating cycle water with regenerant chemicals, resins are removed from the polisher for external regeneration and periodic cleaning.

Nonregenerable powdered resin polishers have found wide acceptance in utility systems. The finely ground resin particles provide good filtration and excellent kinetics for ion exchange. This type of condensate polisher is typically operated at service flow rates of about 4 gpm/ft^2 (10 m^3/[h · m^2]). During cycle cleanup, such as during start-up, an inexpensive cellulose filter aid may be included in the powdered resin mixture. In any case, when the resins become fouled or exhausted, they are discarded.

For either regenerable or nonregenerable polishers, the cation exchange resin can be used in ammoniated form to prevent removal of ammonia from the cycle. Anion resins are in the hydroxide form.

Virtually all once-through boilers, because of their especially high-purity water requirements, employ polishing of feedwater. Many plants polish the total feedwater flow; some polish as little as 20% at full load with increasingly higher portions as load is reduced.

In drum-type boiler systems where water purity is less critical, condensate polishing may not be economically justifiable for normal day-to-day operations. However, even in these systems condensate polishing may be worthwhile, in order to protect the boiler and turbine from the high levels of crud and silica common during initial start-up and subsequent restarts. A polisher can greatly shorten the unit start-up time and often pay for itself in the cost of purchased power that would otherwise be necessary during the start-up period.

Condensate polishing eliminates most deposit-forming materials that create chemical concentration mechanisms in steam generator tubes, but such measures are never completely effective. Long-term accumulations of such deposits, principally iron and copper oxides, on boiler tube surfaces are removed by periodic cleaning. Utility boilers are generally considered "clean" with deposit weight densities less than 5 g/ft^2 (5.4 mg/cm^2) of tube area. Subcritical pressure boilers are considered dirty when accumulations exceed 12 to 40 g/ft^2 (12.9–43.1 mg/cm^2), depending on pressure. Supercritical boilers are considered dirty at accumulations over 12 g/ft^2 (12.9 mg/cm^2). Utility boilers with normal feedwater conditions may be routinely chemically cleaned every three to six years. Many boiler operators minimize cleanings by carefully monitoring deposit weight density in high heat flux areas of the furnace, through tube sampling and analysis during planned maintenance outages.

Corrosion and hydrogen damage of boiler tubes are not likely to occur, where rigorous control of preboiler chemistry, condensate polishing, and periodic cleaning keeps boiler surfaces clean. Since clean tube surfaces cannot be assured at all times, and conditions other than waterside deposits can create chemical concentration mechanisms, it is general utility practice to avoid high concentrations of potentially aggressive sodium hydroxide in the boiler water, less than 1 ppm.

Corrosion of boiler steel is a function of pH (Fig. 33.14), and pH values ideally should fall within a general range of 9.0 to 11.0. A safe value must be achieved without producing excessive residuals of sodium hydroxide. In utility practice, this is accomplished either with a selection of sodium phosphate salts, sodium hydroxide or with a "zero solids" treatment using all-volatile chemicals.

Phosphate treatments (PTs) have been applied to subcritical boilers for decades, and continue to be a primary treatment used in drum boilers today. Historically, there has been a multitude of phosphate compounds and mixtures blended with other treatment philosophies. Some of the traditional PTs such as congruent phosphate treatment (CPT), coordinated PT, and equilibrium phosphate treatment (EPT) have been used over the last 50 years across the fleet of fossil boilers and HRSG evaporators, sometimes successfully, sometimes resulting in tube failures and other problems. Use of CPT, where mono- and/or di-sodium phosphate are used to develop operating control ranges below sodium-to-phosphate molar ratios of 3:1, has resulted in acid phosphate corrosion in certain boilers/HRSG evaporators which have heavy deposits and have experienced phosphate hideout. Use of EPT forced many operators to use very low levels of phosphate (<0.20 mg/l), which essentially provided poor protection

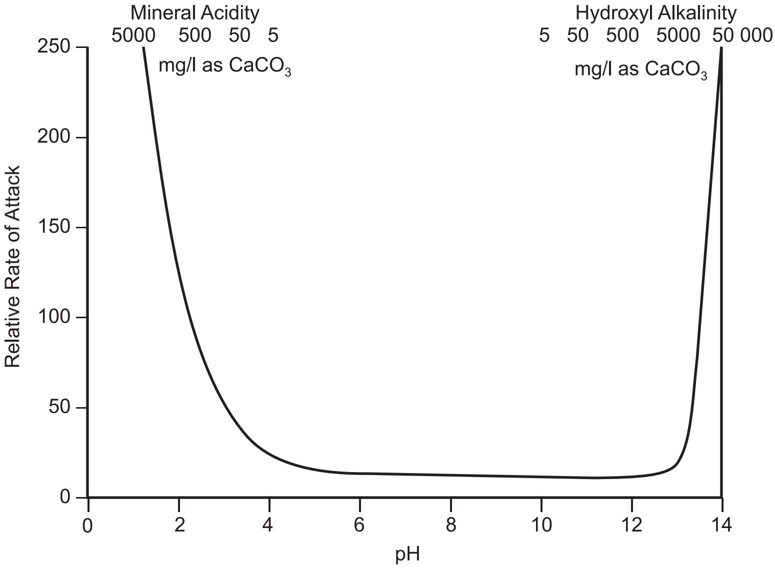


FIGURE 33.14 Relative corrosion rate of boiler steel versus pH and caustic concentration.

in the cases of acidic contaminants from condenser leaks or other sources.

Most recent guidelines from EPRI and others stipulate the use of a blend of trisodium phosphate (TSP) as small additions of sodium hydroxide (caustic) to achieve pH control in drum boilers. The use of monosodium and disodium phosphate is not allowed. This PT is defined by a pH and phosphate control range as shown in Fig. 33.15. The PT range is bounded by sodium to phosphate molar ratio of 3:1 and TSP + 1 mg/l NaOH with a pH above 9.0 and a minimum phosphate limit above 0.3 mg/l. The goal of this treatment is to ensure a solid-alkali-based pH/alkalinity in the boiler or HRSG to provide a noncorrosive pH and neutralize acid forming contaminants such as chlorides and sulfates. Figure 33.16 indicates the areas under risk from tube failure.

Caustic Treatment (CT) is another solid alkali boiler water treatment program. Drum pH is maintained through the addition of sodium hydroxide only. Candidates for CT include boilers with severe phosphate hideout, a history of condenser tube leaks, or saline cooling water. Such systems would not be able to use all-volatile treatment or adequately control PT. Maximum allowed boiler water chloride concentration varies with unit pressure. For example, chloride must be less than 0.3 mg/L if drum pressure is 2500 psia (17.2 MPaa). Sodium hydroxide dosage is 2.5 times the chloride

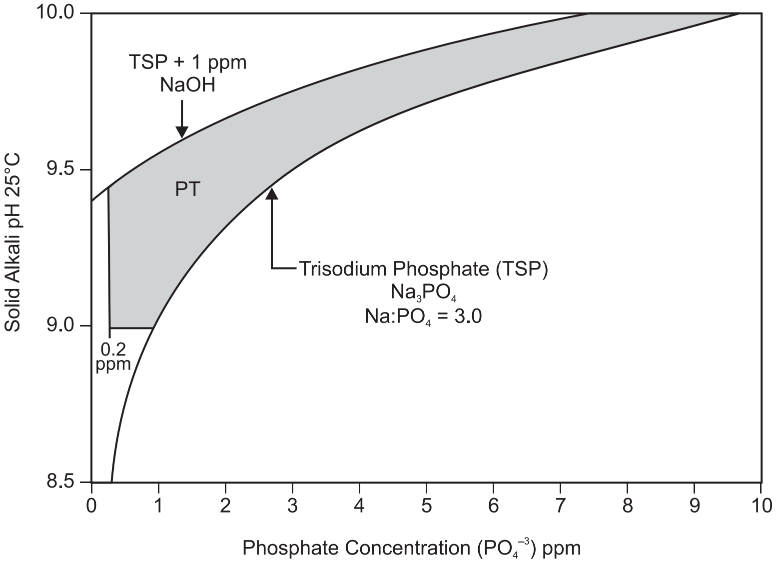


FIGURE 33.15 Operation range for PT. (*Source: EPRI Comprehensive Cycle Chemistry Guidelines for Fossil Plants 2011.*)

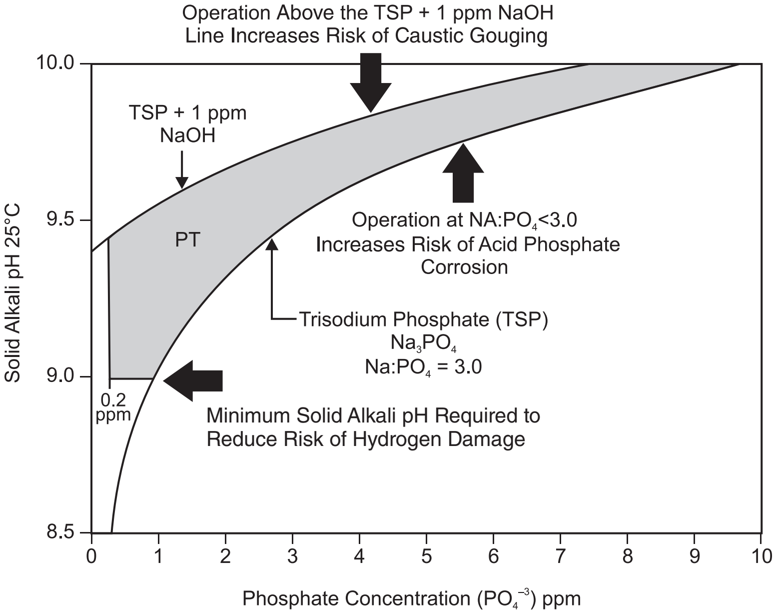


FIGURE 33.16 Operation range for PT including areas identified as risk of tube failures. (*Source: EPRI Comprehensive Cycle Chemistry Guidelines for Fossil Plants 2011.*)

concentration. Sulfate concentration must be less than twice the chloride concentration.

CT programs can be difficult to control; however, and therefore, they require extra diligence to minimize both high and low pH excursions. There are three possible choices employing all-volatile chemistries:

1. All-volatile treatment with reducing agents or AVT(R)
2. All-volatile treatment without reducing agents or AVT(O)
3. Oxygenated treatment (OT)

No solids are added to the boiler or HRSG if all-volatile treatment is used. Since no phosphate or caustic is added to the drums, the feedwater treatment becomes the boiler treatment, providing boiler water pH buffering through the ammonia or amine used for control of the feedwater system pH. As the ammonia or amine pH buffer is weaker than the sodium phosphate or caustic pH buffer of the solids treatment options, the use of AVT requires consistently high-purity feedwater.

It is important to understand the difference between "feedwater" and "drum internal" treatment programs. Both AVT(O) and AVT(R) programs can be used as feedwater treatments, even if phosphate or caustic is added to the drums for internal pH control. It is good practice to differentiate between the two. For example, a plant with copper alloy feedwater heaters would normally utilize AVT(R) feedwater treatment, but could use either phosphate or caustic for boiler internal treatment (PC or CT). If no phosphate or caustic were used, then the drum internal treatment program would also be AVT(R).

Both AVT(R) and AVT(O) are excellent treatment options for drum-type boilers and HRSG, if the feedwater purity will support them. AVT is an excellent choice for systems with condensate polishers, all-steel plants with air-cooled condensers, and a requirement for once-through boilers.

All condensate and feedwater systems in utility steam cycles are treated with all-volatile treatment, as steam attemperation water is taken from the feedwater pump discharge. All-volatile treatment is also the default program for the low-pressure (LP) drum of combined cycle HRSG, when the LP drum acts as an integrated deaerator. In plants of this type, LP boiler water becomes feedwater for the intermediate-pressure (IP) and high-pressure (HP) drums and is used for steam attemperation. Where this is the case, all-volatile treatment is the only option, since no solids (phosphate or caustic) can be present in the attemperation water. AVT is also the default program during steam blows and initial boiler commissioning. AVT is easy to apply and control, providing the feedwater purity remains within specification.

The AVT(R) program must be used for systems containing copper alloy feedwater heaters, where a reducing environment is required to minimize corrosion. Primary pH control is achieved with either ammonia or amine. Passivator (generally either hydrazine or carbohydrazide) is used to control the reducing environment in the condensate-feedwater system.

The AVT(O) program is used for all-steel systems, and no passivator is typically fed. In some cases, a reduced level of passivator can be used or in some cases a small amount of DO may have to be added. The presence of small amounts of DO promotes the formation of a more adherent iron oxide passivation layer and lowers the potential for FAC. The need for passivator feed in all-steel plants can best be determined through a detailed soluble and insoluble iron transport study.

Both AVT(R) and AVT(O) treatments require very high-purity feedwater at all times. Feedwater cation conductivity must remain less than 0.2 µS/cm, and DO at the condensate pump discharge must remain less than 10 µg/L.

OT is the third treatment option for all-steel systems with condensate polishers. OT minimizes corrosion of all-steel systems by promoting the formation of mixed iron oxides to form a more tightly adherent passivation layer. It results in lower metal transport and minimizes the need for chemical cleaning. OT is the preferred treatment for most supercritical boilers. It is also a strong candidate for drum-type units with all-steel construction, and full-flow condensate polishers or air-cooled condensers.

OT requires extremely high-purity makeup, high-purity condensate, and extremely tight control. OT programs will be corrosive, if contamination of the feedwater provides the electrolyte necessary to support the corrosion reaction. Many systems otherwise meeting the criteria for OT cannot achieve the tight control required. Cation conductivity must always be less than 0.15 µS/cm, without exception. OT is extremely effective in the right situation and is the first treatment choice, if the unit meets the criteria.

As stated earlier, a disadvantage of AVT for drum-type boilers is that the boiler water is lightly buffered, and in the event of feedwater contamination, is subject to significant and rapid pH excursions. There is no tolerance for condenser cooling water inleakage, unless condensate polishing is provided.

Contaminant salts entering the cycle from other sources may produce acids or alkalis capable of being concentrated locally to corrosive levels. Typical contaminant sources are:

- Condenser leakage
- Treated makeup water contamination by evaporator carryover or demineralizer leakage
- Regenerant contamination from ion exchange units
- Incomplete removal of chemical cleaning solvents or alkalis

Of these, condenser leakage is the most significant. Boiler tube hydrogen damage that results from condenser leakage is particularly likely to occur, where the cooling water is brackish. The reactions of contaminants such as calcium chloride and magnesium chloride in boiler water, after depletion of any soluble phosphates, are:

$$MgCl_2 + 2H_2O \rightarrow Mg(OH)_2 + 2HCl \tag{33.6}$$

$$CaCl_2 + 2H_2O \rightarrow Ca(OH)_2 + 2HCl \tag{33.7}$$

In high-purity unbuffered boiler water, very small cooling water leaks can reduce pH to 4 or less. Where the acid is concentrated locally within a deposit at a tube surface, corrosion and hydrogen damage proceed rapidly. While protection is afforded by condensate polishers, strict surveillance of condenser leakage is prudent for drum-type boiler cycles without polishers. Generally, leaks causing 0.5 mg/L (total chloride and sulfate) feedwater concentrations can usually be accommodated in normal operation without serious difficulty. Feedwater concentrations of 2 mg/L of total chloride and sulfate may be tolerated for short periods, but immediate boiler shutdown is usual when a condenser leak produces concentrations greater than this. Immediate boiler shutdown is always indicated where acceptable boiler water pH cannot be maintained.

The necessary continuous surveillance of condenser leaks usually relies on cation conductivity monitoring, which effectively senses concentration changes as small as 2 µg/L. In this method, a condensate sample passes through a column of acid-form cation resin to convert sulfate, chloride, and nitrate salts to more electrically conductive sulfuric, hydrochloric, and nitric acid. The conductivity is then measured in the resin-treated sample.

Monitors for silica and sodium are alternative devices for detection of condenser leaks. Against background concentrations commonly encountered in turbine condensates, available monitoring equipment can reliably detect changes of 20 µg/L or less in either of these contaminants.

Steam Phase Problems

In the 1950s, it became apparent that the silica in steam that was causing deposits on the LP stages of utility turbines was not carried out of the boiler in droplets of the boiler water, but rather it was a gaseous fraction of the high-temperature vapor. (This was a contribution to water chemistry from the field of geology.) Previously, it had been long recognized that carbonates would break down to yield carbon dioxide (CO_2) in steam, but now, there was growing evidence that minerals might actually volatilize and leave the boiler in the gas phase too. With development of the once-through boiler, it was apparent that any minerals in the feedwater, volatile or not, would be passed along to the turbine and condenser. This led to the development of polishing demineralizers for the condensate stream to prevent buildup of minerals in the cycle that would lead to deposits. It also led to development of AVT, or the use of volatile chemicals such as ammonia and hydrazine, as the only chemical treatment applied to the cycle.

The purity of makeup improved greatly in the succeeding years. Demineralizers replaced evaporators not only based on economics but also on quality. Evaporators (as then designed) were unable to produce the low silica levels needed to avoid turbine deposits.

The newer systems began to experience turbine blade cracking, generally occurring on the last two wheels, and it was found that the cracking was caused by caustic. Furthermore, ammonia concentrations and pH were difficult to control, because the polishing demineralizer removed ammonia (usually causing an increase in sodium) and erratic control often led to attack of copper alloy heater tubes.

Because of these problems, it became necessary to study steam-phase conditions throughout the cycle. This required the development of sophisticated and reliable isokinetic sampling systems capable of handling both superheated and wet steam, at high pressure and under vacuum. Analyses were made of the nature and causes of system deposits, and basic research was undertaken in the physical chemistry of the elements and compounds found. In response, limits were placed on sodium, chloride and sulfate levels, because these seem to be the major cause of stress corrosion cracking and corrosion fatigue attacks on turbine blading, a problem more common to AVT systems than to drum-type boilers using PT.

There is still more to be learned about vapor-phase chemistry, but present state-of-the-art calls for extensive sampling and continuous analysis of makeup, condensate, deaerated water, feedwater at the economizer inlet, boiler water, superheated steam, and selected stage heater drains. The analyses include continuous measurement of conductivity, pH, DO or room temperature ORP, sodium, and silica (on demineralized makeup); iron, copper, and nickel on feedwater, heater drains, and condensate; ammonia before and after condensate polishers; hydrazine or passivator on feedwater; and boiler water testing (with drum-type boilers). With this type of monitoring, conditions can be continuously scrutinized both during steady load and during shutdown and start-up, so that corrective adjustments can be made in chemical treatment, or operating problems (demineralizer regeneration, control of air inleakage, control of condenser leakage, etc.) can be corrected.

Subsequently, it was found that even if the low levels of sodium, chloride, and sulfate were maintained in the steam, that deposits may still form on the LP stages, but that it wasn't until out of service conditions exposed these deposits to an oxygenated liquid or humid environment, that the corrosion processes were initiated. Today then improved lay-up protection for turbines is recommended using nitrogen or dehumidified air to prevent LP turbine corrosion.

The steam-phase chemistry relative to geothermal plants is completely different from conventional plants, as the vapor often contains additional contaminants (e.g., boron and sulfur compounds) at parts per million (mg/L) rather than parts per billion (µg/L) levels.

Water Chemistry in Nuclear Plants

The nuclear PWR (Fig. 33.4) has two major water systems:

1. The primary loop or reactor coolant system
2. The secondary loop or steam generator-turbine cycle

Components of the primary loop are the reactor vessel, a pressurizer, steam generators (heat exchangers), and circulating pump. In the primary loop, water temperature is allowed to rise only about 50°F (28°C) passing through the reactor, so recirculation rates are quite high to absorb the amount of heat generated. Pressure of the recirculating water is kept high enough to keep the water from boiling. The pressurizer maintains this pressure and absorbs changes in volume produced by changes in temperature. For maximum corrosion resistance, wetted surfaces in the primary loop are usually stainless steel or nickel-based alloys.

High purity must be maintained in the primary loop water to minimize fouling of reactor and exchanger heat transfer surfaces, and to avoid contaminants that could form undesirable radioactive isotopes under neutron flux. Controlled additions and removals of boric acid in the primary loop water provide the correct concentration of neutron-absorbing boron needed to control neutron flux and energy transfer. Chemicals such as lithium hydroxide, forming relatively safe radioisotopes under neutron flux are used for pH control in the primary loop.

Under nuclear radiation in passage through the reactor, some of the primary loop water is decomposed into hydrogen and oxygen as follows:

$$H_2O \rightarrow H_2 + \frac{1}{2}O_2 \tag{33.8}$$

To suppress oxygen generation and to scavenge oxygen entering the system, hydrogen gas is commonly added. Primary loop water purity is usually maintained by continuously passing a portion of the circulating water through a mixed bed demineralizer. These generally utilize anion resins in the borate form, to avoid removal of boron from the water. As impurities accumulate, these resins tend to become radioactive and regeneration becomes impractical. The resins are disposed of as a solid radioactive waste.

Two basic heat exchanger designs are employed as secondary loop steam generators in PWR systems. The recirculating U-tube type (Fig. 33.17) is analogous to a drum-type boiler in a fossil-fuel system. Having an internal recirculation rate of 3 to 4 times the steam flow, the unit provides mechanical water separation and continuous blowdown. However, it differs from fossil-fuel boilers in that there is no provision for superheating the steam.

The other PWR heat exchanger design (Fig. 33.18) provides once-through-type steam generation. The heat exchanger is baffled so that

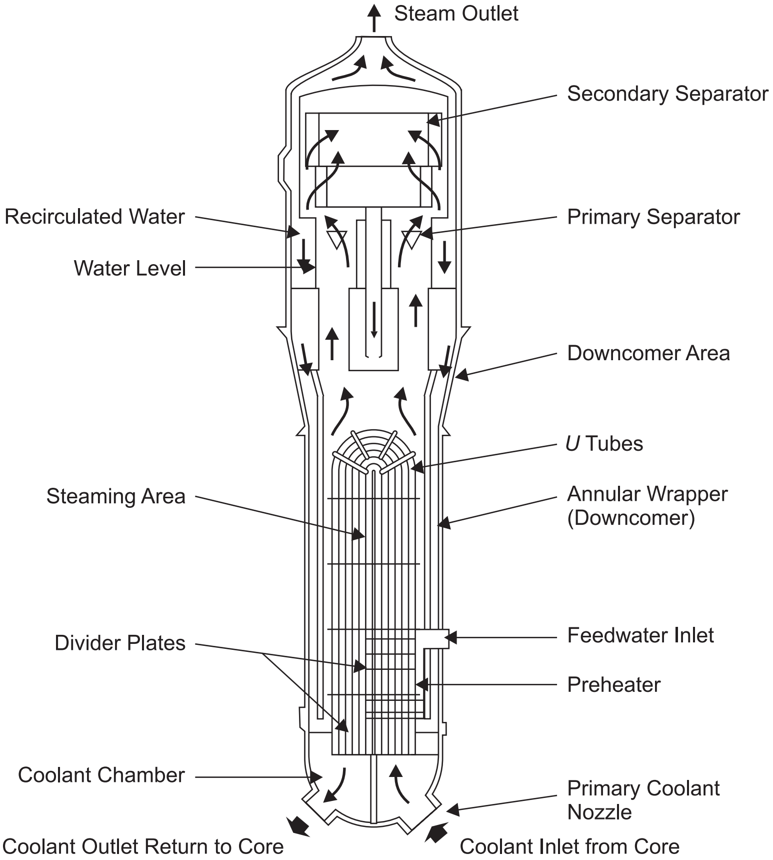


Figure 33.17 PWR vertical U-tube recirculating-type steam generator with integral feedwater preheater.

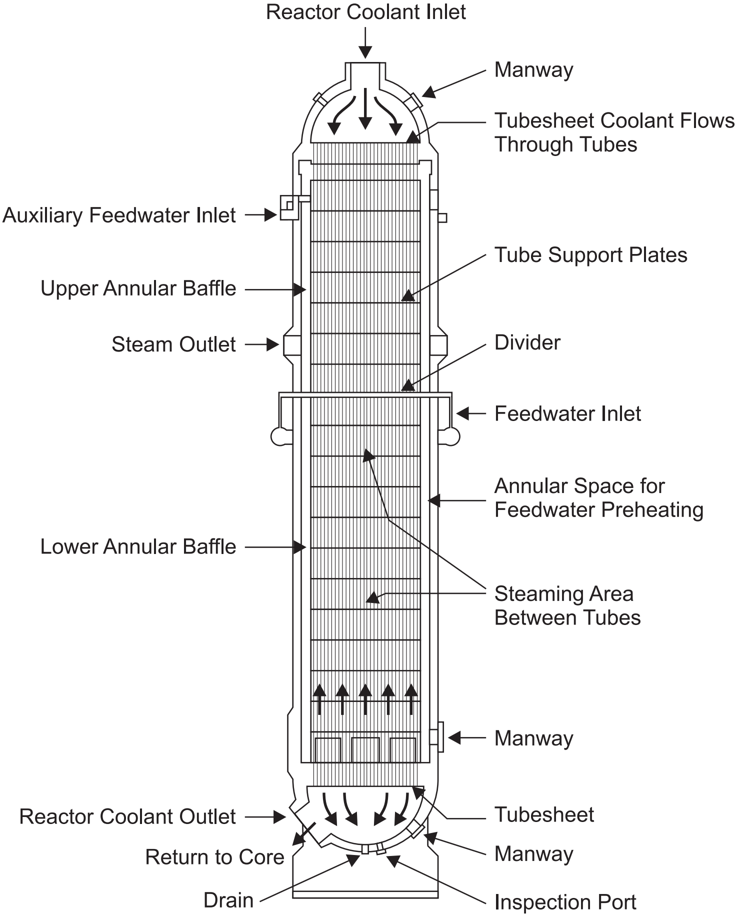


Figure 33.18 PWR once-through-type steam generator. (*Adapted from Steam—Its Generation and Use, Babcock and Wilcox Company, 1972*.)

incoming feedwater first flows down through an outer annulus in which it is heated to saturation temperature, and then it is converted totally to steam and is slightly superheated in a single upward shell-side pass through the tube bundle. Depending on load, up to about 60°F (33°C) superheat can be achieved.

Either type steam generator requires maximum corrosion resistance on the primary side, so tube materials are commonly special nickel-iron-chromium alloys (e.g., alloys 600, 690, and 800). Carbon steel shells are generally used, although those parts of the shell surface constituting the primary coolant inlet and outlet plenums are clad on the coolant waterside.

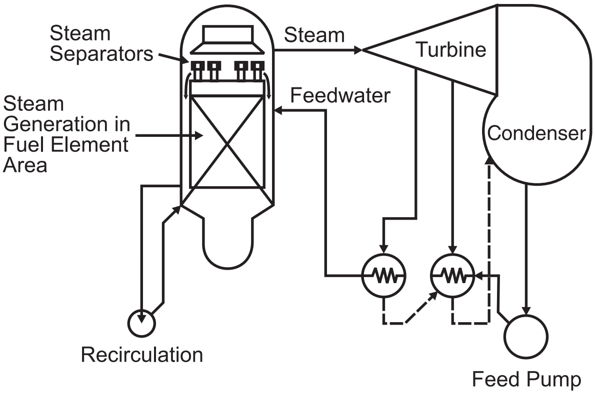


Figure 33.19 In a BWR, steam is generated in the same vessel that contains the fuel elements, as shown in this simplified diagram.

AVT treatment is commonly practiced for all types of nuclear PWRs. Ammonia, as well as low-volatility organic amines (monoethanolamine, methoxypropylamine, or morpholine) are in common use. The low-volatility amines are present in higher concentrations in the moisture separator reheater drains of the PWR, providing a higher pH and lower corrosion as a result. This application has reduced corrosion product transport to the steam generators.

In the nuclear BWR (Fig. 33.19), boiling occurs in the reactor itself. The same water serves as the cycle working fluid, the reactor coolant, and the nuclear reaction moderator. BWRs are comparable to drum-type boilers. A portion of the water passing through the core is converted to steam. The steam-water mixture is then separated, with the steam going to the turbine and boiler water returning through circulating pumps to the core inlet.

An important aspect of BWR operation is the effect on the working fluid of direct exposure to nuclear radiation. Some of the water is decomposed into hydrogen and oxygen. It is not possible to inject hydrogen as in the PWR, because of the need for continuous removal of all noncondensable gases at the condenser to maintain the vacuum required for turbine efficiency. Thus, steam produced by a BWR reactor contains high concentrations of oxygen, an important factor in corrosion.

Nitrogen entering the cycle by air inleakage or decomposition of nitrogenous compounds can react to form nitric acid:

$$5O_2 + 2N_2 + 2H_2O \rightarrow 4HNO_3 \tag{33.9}$$

Additives for pH control and oxygen scavenging such as amines and hydrazine are not usable in BWR cycles, because they are subject to nuclear decomposition. Thus, corrosion control relies primarily on the corrosion resistant materials used throughout the cycle.

Metallic contaminants in the cycle water, either from condenser leakage or corrosion of system metals, are subject to stringent limitations to avoid formation of hazardous isotopes and to avoid deposition of crud on the core heat transfer surfaces. Copper is specifically limited, because of its tendency to foul the orifices of the reactor core water distributor. Makeup water is demineralized to less than 0.1 µS/cm specific conductivity and 10 µg/L silica. Full flow condensate demineralization is then employed to maintain cycle water purity at limits established by the reactor manufacturer. Typical limits are 30 µg/L total metals, 2 µg/L Cu, 2 µg/L NaCl, and 0.1 µS/cm conductivity at 25°C. Resultant feedwater is essentially neutral, with pH equal to 7.0.

Where deep bed demineralizers are used in BWR condensate polishing, resins are usually sluiced to external vessels for scrubbing and regeneration. The regenerant wastes generally contain low-level radioactivity, which requires processing in the liquid radwaste system. Where nonregenerable powdered resin units are used for polishing, the spent, sluiced resin must be processed.

Blowdown Control

The primary factors that limit COC in HP boiler waters are total dissolved solids (TDS) and silica.

TDS are limited primarily to ensure steam purity. Limits are more stringent at higher drum pressures, because of the decreasing steam-water density differences that tend to increase mechanical carryover percentages (see Fig. 33.20). Boiler water specific conductance has a reasonably constant proportional relationship to dissolved solids and is the parameter most commonly monitored and controlled.

To prevent silica from selectively carrying over (volatilizing), silica is kept below prescribed maximums for steam turbine operation. Silica volatility increases almost exponentially with boiler water pressure. Drum boiler water silica limits thus decrease sharply as pressure increases (see Fig. 33.21).

Actual boiler water COC must be determined in order to calculate chemical mass balances and operating economics. However, in high-purity feedwater/boiler water systems, determining COC presents a challenge. Blowdown is rarely metered directly. In addition, feedwater and steam flow meters (where available) often lack the calibration accuracy and precision necessary to determine (by difference) the very small blowdown flows reliably. In LP systems, chemical ions in the feedwater can be used to determine boiler water COC analytically; however, the concentrations of such ions in HP boiler feedwater are typically below detectable limits, and the

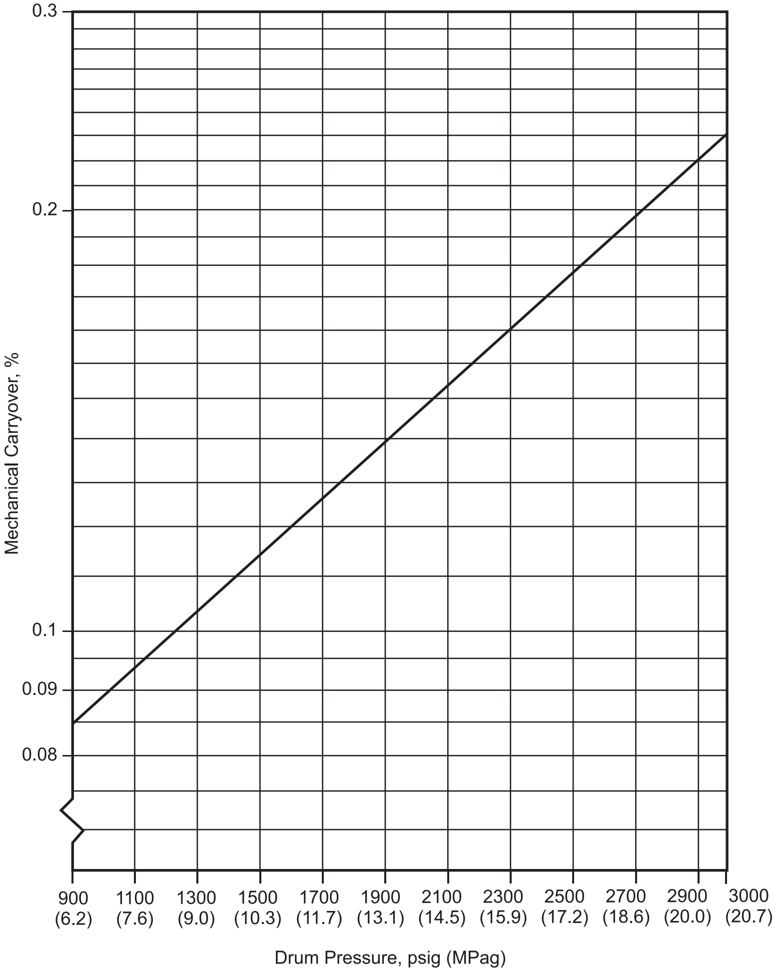


Figure 33.20 Mechanical carryover versus drum pressure.

conductivity of the boiler water is predominately from the chemicals added to the system. If they are detectable, the concentrations are so low that even a small analytical error could cause a 50 to 100% error in calculating COC.

Blowdown flow rates can sometimes be estimated with reasonable accuracy for systems in which continuous blowdown valves with known orifice sizes are used. Valve manufacturers generally supply curves showing pounds per hour (kg/h) blowdown flow versus pressure drops for each setting of the valve. Typically, the pressure drop (ignoring piping losses) is the boiler drum pressure minus the operating pressure of the blowdown flash tank or receiver.

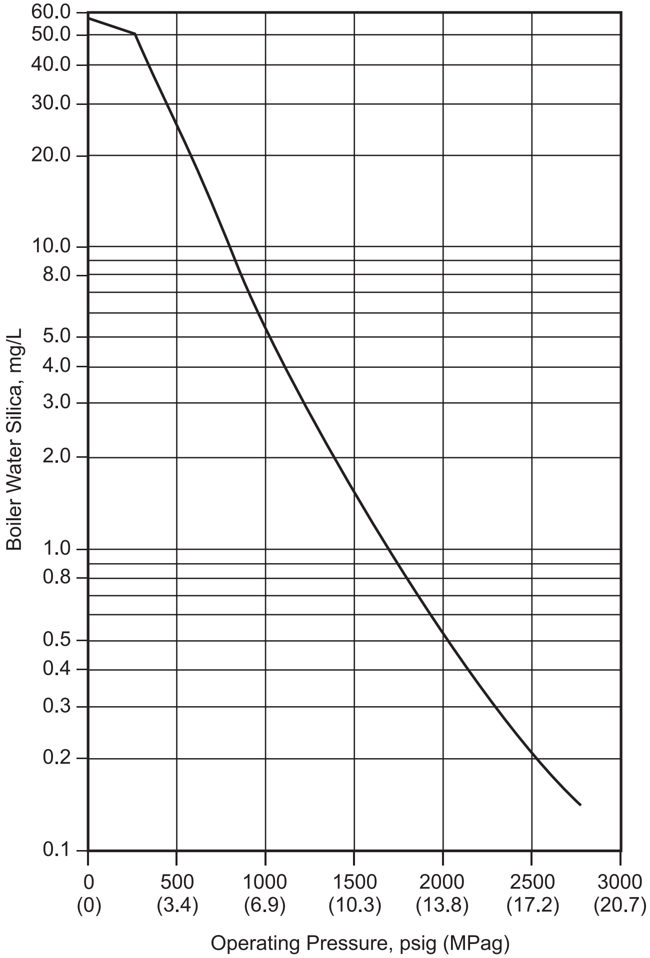


FIGURE 33.21 Recommended maximum boiler water silica concentration at pH 11.3 so as not to exceed 20 µg/L silica in steam.

Blowdown flow thus determined (in conjunction with either metered feedwater or steam flow rate) is then used to determine feedwater concentration ratio in the boiler.

Nonvolatile tracer ions can be used to determine boiler water COC. A known flow proportional concentration (e.g., 1 mg/L) of the tracer is metered to the feedwater until it reaches its equilibrium concentration in the boiler water. The cycles of boiler water concentration are then derived from the determination of relative concentrations of the tracer ion in the feedwater and boiler blowdown.

Another method for determining cycles of high-purity boiler water concentration is to make a slug addition of an arbitrary amount of suitable ion (soluble, nonvolatile, and accurately measurable). Because the decay of this species will be exponential, its concentration in the boiler at any time will be a function of boiler volume and blowdown rate. This relationship is shown in Eq. (33.10):

$$\ln C_t = -(\mathrm{BD}/V)t + \ln C_i \qquad (33.10)$$

where C_i = initial concentration, mg/L
C_t = concentration at time t, mg/L
t = time interval between C_i and C_t, hours
V = boiler volume, lb (kg)
BD = blowdown flow rate, lb/h (kg/h)

Once the blowdown rate is determined, the feedwater rate can be calculated using Eq. (33.11):

$$\mathrm{FW} = S + \mathrm{BD} \qquad (33.11)$$

where FW = feedwater flow rate, lb/h (kg/h)
S = steam flow rate, lb/h (kg/h)

The COC can then be calculated using Eq. (33.12):

$$\mathrm{COC} = \mathrm{FW}/\mathrm{BD} \qquad (33.12)$$

Condenser Cooling Water

The thermal efficiency of modern fossil-fuel steam electric plants averages less than 35% for subcritical units, up to 45% for supercritical units, and 65% for combined cycle power plants. The largest part of the thermal loss, equal to about 50% of the steam energy, is rejected at the condenser as the steam is condensed to water and releases its heat of vaporization. Nuclear plants, averaging about 32% efficiency, lose even more heat at the condenser. Heat rejected at the condenser is transferred to cooling water, which subsequently releases this heat to the environment. Air-cooled plants release the heat directly to the air.

Although water circulating through the tubes of a surface condenser is called cooling water, it is important to recognize that there is no cooling of the vapor or condensate. The circulating water simply absorbs the heat of vaporization of steam leaving the turbine, converting it to liquid at the same temperature.

The primary function of a surface condenser is to maximize cycle efficiency by allowing steam to expand through the turbine to the lowest possible exhaust temperature and pressure. Just as in a boiler drum, the temperature of steam and water in a condenser is directly related to pressure. At 102°F (38.9°C), for example, the corresponding saturated steam pressure is about 1.0 psia or 2.0 in. Hg (6.9 kPaa). At this pressure, 1 lb of steam occupies 333.69 ft^3 (20.83 m^3/kg), but when condensed, it occupies only 0.016 ft^3 (0.001 m^3/kg), about 0.005% of the original steam volume. The pressure in the condenser is often referred to as the "back pressure."

Noncondensable gases (air, ammonia, etc.) in the condenser increase pressure and reduce the vacuum achievable, and such gases are continuously removed by mechanical vacuum pumps or steam jet air ejectors (see Fig. 33.12).

The ability of a surface condenser to provide the lowest possible back pressure for a given turbine load and cooling water temperature is adversely affected by such things as follows:

- Waterside scaling and fouling of condenser tube surfaces
- Partial blockage of cooling water flow through the tubes
- Inadequate removal of noncondensable gases
- Faulty distribution of exhaust steam

Waterside scaling and fouling are probably the most common causes of impaired condenser performance.

The effect of a 1.0 in. Hg (25.4 mm Hg or 3.4 kPaa) rise in back pressure in a 500 MW plant is illustrated in Table 33.2. A back pressure

500 MW Generation, Coal Fired, 1.5 in. Hg (38.1 mm Hg) Design Back Pressure*		
Actual back pressure in. Hg (abs) mm Hg (abs)	 2.5 63.5	 3.5 88.9
Change in heat rate Btu/kWh kJ/kWh	 200 211	 400 422
Additional fuel at 90% boiler efficiency million Btu/h million kJ/h	 111 117	 222 234
Additional fuel cost at $1.5/million Btu at €1/million kJ	 $3996/day €2808/day	 $7992/day €5616/day
Additional carbon dioxide released to environment at 210 lb CO_2/million Btu at 90 kg CO_2/million kJ	 23 310 lb/h 10 530 kg/h	 46 620 lb/h 21 060 kg/h

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*Unit rating permits fixed load maintenance.

Table 33.2 Effect of Turbine Back Pressure Increase on Plant Efficiency increase in this magnitude can decrease electrical output by 1 to 3%. A plant may avoid the loss of production by increasing the steam flow through the turbine, but this will come at the cost of higher heat rate, higher fuel consumption, and higher emissions. Effective condenser water treatment is a very important factor in preventing such losses.

Seven basic types of condenser cooling systems are used in utility stations:

1. Once-through cooling
2. Cooling lake and cooling pond systems
3. Spray ponds
4. Wet cooling tower systems
5. Air-cooled condensers
6. Wet-dry combination cooling tower systems
7. Wet surface air coolers (WSAC)

In once-through cooling, water passes once through the condenser and returns to its source at a higher temperature. Because residence time and temperature are low, scaling is usually not a problem, although calcium scales can form with some waters. The principal fouling problems in once-through systems are usually related to microbial activity and silt deposition. Regularly scheduled biocide control usually achieves a moderate increase in condenser cleanliness for several hours. Application of a biodispersant with each application of chlorine or bromine can increase both the magnitude and duration of this improvement (Table 33.3). By increasing the effectiveness of chlorine or bromine, such biodispersants also can reduce the dosage of biocide, helping the plant meet discharge regulations.

	Cleanliness Factor Improvement	
Treatment	**Highest Percent**	**Duration***
0.05 mg/L Cl_2 residual plus 15 mg/L biodispersant	7.24%	6.5 hours
12.12 mg/L Cl_2 residual plus 5 mg/L biodispersant	2.61%	6 hours
12.4 mg/L Cl_2 residual alone (no biodispersant)	0.55%	2 hours

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*Short duration treatment applications with system blowdown closed until chlorine residual dissipated.

Table 33.3 Condenser Tube Cleanliness Factor Improvement Using a Biodispersant

With the advent of environmental regulations restricting thermal discharges, some once-through systems have been modified so that the condenser outlet water passes over a "helper" or thermal abatement cooling tower or through a tempering canal with floating spray modules to dissipate heat before final discharge. Since such helper additions follow the condenser, biocide and dispersant treatment of the water are the same as for conventional once-through systems.

Cooling water may be discharged to cooling lakes, which are artificial impoundments that are created by damming a stream. Condenser water is recirculated through the lake, and heat is dissipated primarily by surface evaporation. The lake receives makeup from rainfall and runoff from its drainage area. Cooling lakes make it possible to service high cooling water flow requirements from streams too small to provide such cooling capacity on a once-through basis.

By contrast, cooling ponds are defined as impoundments that do not impede the flow of a navigable stream. They are usually constructed along a stream from which makeup water may be pumped to meet evaporative losses not replaced by rainfall or runoff from surrounding drainage areas. Cooling ponds contained within earthen levees at levels above the surface water are said to be "perched." The area required for natural evaporation is typically about 1 to 1.5 acres (4000–6000 m^2) per megawatt of capacity. A pond typically provides detention of about 5 to 15 days to produce the necessary heat dissipation.

Blowdown from cooling ponds is composed of bottom seepage and controlled overflow to the source stream. Because of the large rainfall-receiving surface areas, concentration ratios are typically quite low, up to about two times source concentration. Even such low concentration increases may be significant in terms of reduced calcium carbonate solubility, so condenser tubes are more likely to scale on pond systems than on once-through cooling systems. Scale inhibitors and dispersants are commonly applied to cooling pond systems to prevent deposition in the condenser and auxiliary cooling systems. Acid and carbon dioxide have been applied in unusual cases of high-scaling potential.

A significant aspect of cooling ponds is that they support a variety of aquatic organisms. They often have large fish populations. Specific dispersants in conjunction with periodic feed of chlorine or bromine may be needed to keep condenser tubes free of biological slimes, initiated by the microorganisms in the pond.

Spray ponds promote evaporation by mechanically dispersing water into sheets and droplets, dissipating heat more effectively so that less pond area is required. Evaporation is mechanically promoted, so it is less dependent on climatic conditions. Recirculating water treatment requirements generally correspond more closely to those of evaporative (wet) cooling towers than to cooling ponds or lakes.

Where large cooling ponds or spray ponds are impractical, cooling towers are installed to reduce thermal pollution of receiving waterways.

To comply with restrictions on thermal discharge, blowdown is taken from the tower basin, having the lowest temperature of the recirculating system.

An important advantage of wet cooling towers is their ability to significantly reduce raw water withdrawal and wastewater discharge (Table 33.4).

Because drift (entrainment of fine mist) from a cooling tower is part of blowdown, the net discharge to the receiving stream in this example would be about 10 to 200 gpm (2.3–45 m^3/h) less than the 2000 gpm (454 m^3/h) shown.

With the increased planning for maximum water conservation, coal-fired plants may substitute cooling tower water for raw water for ash sluicing. The heat of bottom ash evaporates some sluice water, the ash retains a small amount, and the final volume of wastewater for disposal is further reduced.

Zero liquid discharge has been designed into many power plants to conserve water and reduce environmental impact. There are many strategies for implementation of zero liquid discharge from a power plant. The system may be as simple as operation at high COC in the condenser cooling system, followed by a solar evaporation pond, or as complex as a multiprocess treatment system with softening, RO, evaporation, and crystallization. In all cases, maintenance of the plant water balance is critical to the successful operation of the system.

Various processes for sidestream treatment of cooling water and for blowdown concentration, reduce final discharge volume and required evaporation pond areas. One such conceptual system is illustrated in Fig. 33.22. Although sidestream processing can control concentrations of potentially scale-forming ions, high salinity in the recirculating water is characteristic of these treatment schemes. The effects of high dissolved solids in cooling tower drift and on

	Once-Through Cooling System	**Wet Cooling Tower Recirculating System***
Condenser flow, gpm (m^3/h)	400 000 (90 850)	400 000 (90 850)
Evaporative concentration ratio	1	5
Makeup water flow, gpm (m^3/h)	400 000 (90 850)	10 000 (2271)
Discharge water flow, gpm (m^3/h)	400 000 (90 850)	2000 (454)

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*Based on 20°F (11°C) temperature rise and evaporation factor of 1.

TABLE 33.4 Water Flows for 1000 MW Condenser Cooling System

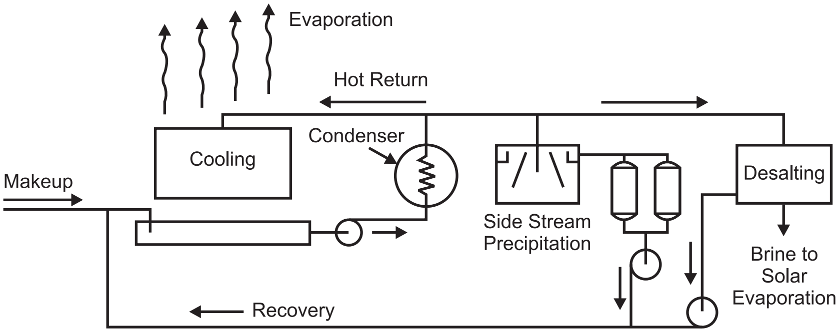

Figure 33.22 Simplified schematic of process to recover cooling water by sidestream treatment and desalination to yield only a concentrated brine for evaporation.

surrounding vegetation and structures must be considered. Cooling water TDS may be limited by air emission standards. In addition, the significantly greater impact of condenser leaks on the chemistry of the boiler water cycle must be addressed.

Air-cooled condensers or "dry" cooling systems are an increasingly popular option for plants sited in water-short regions, or in populated regions where cooling tower plume and drift are a concern. Moisture plumes emanate from cooling tower stacks like clouds under many weather conditions, literally dominating the atmosphere in the immediate vicinity. One means of eliminating plumes is to use nonevaporative dry cooling towers. In dry cooling towers (Fig. 33.23), heat is transferred from the recirculating water to the air by convection rather than by evaporation.

Figure 33.23 Typical dry cooling tower. (*Courtesy of SPX Cooling Technologies, Inc.*)

Figure 33.24 Large combination wet-dry tower used to cool condenser water. (*Courtesy of SPX Cooling Technologies, Inc.*)

The ambient air temperature controls dry cooling tower performance, rather than wet bulb temperature as for wet cooling towers, and turbine backpressures are higher for dry tower systems than for wet towers. Therefore, the plant heat rate is higher. Combinations of wet and dry cooling towers (Fig. 33.24) may be used to advantage to alleviate plume problems with minimum loss of cycle efficiency. In addition, since dry towers handle their part of the heat load without evaporation, overall makeup and blowdown volumes are less for wet-dry cooling tower combinations. Systems may be set up with the recirculating water flowing in either series or parallel through the wet and dry towers. Designs usually provide for a means of totally or partially bypassing either air flow or recirculating water flow selectively around either the wet or dry tower, as may be required to optimize plant efficiency for varying plume abatement and water conservation requirements. Figure 33.25 illustrates an integral wet-dry cooling tower unit with provision for adjusting the balance of airflow through the wet and dry sections. Recirculating water treatment practices for wet-dry cooling tower systems are essentially the same as for straight wet cooling tower systems.

WSAC may be used instead of traditional dry and open recirculating cooling water systems. For the same heat load, WSAC typically use 75% less energy than dry systems and 25% less energy than open recirculating systems. In addition, WSAC can operate at higher COC than standard cooling towers, because they are less susceptible to suspended solids fouling. Some mineral precipitation is expected. WSAC can receive blowdown from traditional cooling towers as

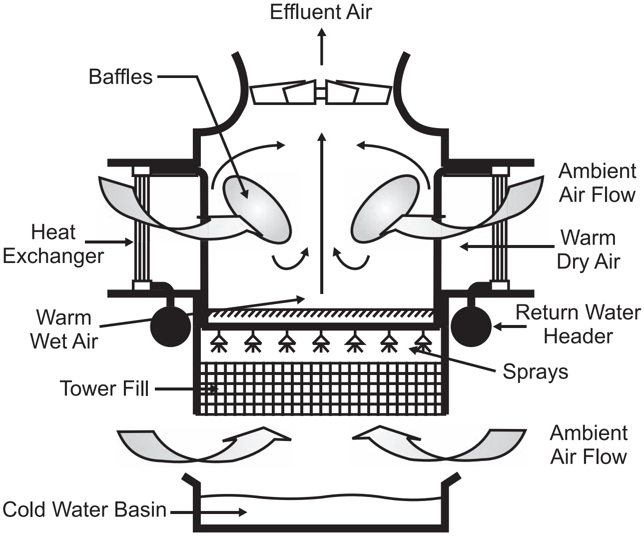

Figure 33.25 Integral wet-dry cooling tower with damper control. (*Courtesy of SPX Cooling Technologies, Inc.*)

makeup water and concentrate it further, beyond mineral solubility limits, further reducing wastewater discharge.

WSAC applications in power plants may include steam condensing, auxiliary cooling, and gas turbine air inlet cooling. Air is induced downward over the tube bundle, which is located within the actual cooling tower structure. Water flows downward along with the air. Heat from the process stream is released to the cascading water, and heat is transferred from the cascading water to the air stream via evaporation. The air stream is forced to turn 180°, providing maximum free water removal. The fans discharge air vertically at a high velocity to prevent air recirculation. The deluge effect provided by the water cascade directly over the tubes minimizes the propensity for suspended solids fouling and mineral precipitation on the tubes, thus allowing operation at higher COC.

Closed recirculating water systems handle a variety of cooling requirements in utility stations, avoiding introduction of outside contaminants that might foul heat exchanger surfaces. Systems of this type are sometimes used for cooling the hydrogen circulated for electric generator cooling. They also may be used for cooling of compressed air, jacket cooling for standby diesel engines, and for certain lube oil cooling requirements. In nuclear plants, closed recirculating cooling water systems are commonly used to handle heat loads from the reactor vessel shielding, primary coolant pump seal housings, and other heat loads within the reactor building.

Ash Handling Systems

Another major water use in coal-fired power plants, and to a lesser extent in oil-fired plants, is ash transport. The solids that fall to the bottom of the boiler furnace (bottom ash) are usually cooled and conveyed from the boiler by water. The solid products of combustion (fly ash) in the flue gas that do not deposit in the boiler convection passes or air heater are subsequently removed by electrostatic precipitators, bag filters, or wet scrubbers. Fly ash accumulations are removed from these devices either by water, or by mechanical or pneumatic means.

The quantity of water required for ash sluicing varies with design factors such as method of firing and nature of the coal. For a typical 1000 MW coal-fired plant, it amounts to about 10 mgd (1600 m^3/h).

For molten slag tap or "wet bottom boilers," where water is used to quench molten ash, heat pick up can be in the range of 1 million Btu (1 GJ) per ton (0.9 metric ton) of bottom ash. Suspended solids in bottom ash water are of concern, if they are difficult to settle, and may be very abrasive to the ash sluice pumps. Coagulants may be needed to reduce supernatant turbidity. Dissolved solids contribution to the sluice water from the ash will vary with the nature of the ash. In some cases, the sluice water will become very alkaline and scale forming.

Fly ash is much more leachable and may contribute 50 to 800 mg/L dissolved solids to the transport water. Fly ash often contains hollow microspheres (Figs. 33.26 and 33.27), which are difficult

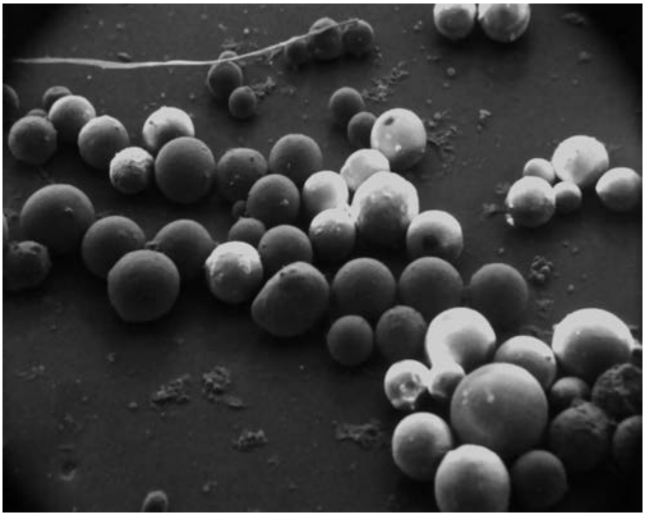

Figure 33.26 The suspension firing of coal produces slag in a variety of forms, including these microspheres, which float to the surface of wet ash collection ponds. Random spheres.

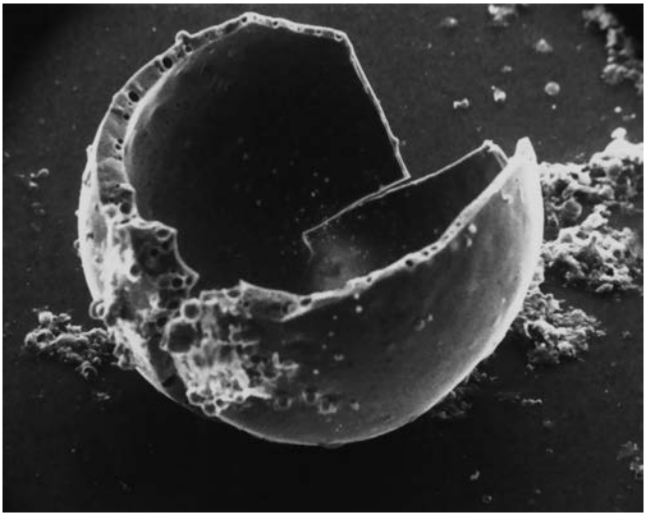

FIGURE 33.27 The suspension firing of coal produces slag in a variety of forms, including these microspheres, which float to the surface of wet ash collection ponds. Broken shells.

to separate from sluice water by sedimentation. Dry transport systems are often used to handle fly ash to avoid the issue of the floating microspheres (also called centispheres).

In oil-fired plants, ash is produced in comparatively small quantities. Bottom ash removal from the boiler by fireside washing and sluicing may be needed only occasionally. Oil ash generally does not settle in ponds as well as coal ash. While oil ash pond overflow waters have many of the same characteristics as in coal-fired plants, high concentrations of vanadium may be present, originating as an ash constituent of some fuel oils. Bottom ash in some oil-fired plants is removed by dry collection rather than by water sluicing.

Where there is a market for the bottom ash, or where insufficient land is available for settling, dewatering bins can be used and the dewatered ash trucked away. Water drainage from dewatering bins or the supernatant from ash ponds can be recycled to the sluice pumps. Makeup to such recycle systems is required for replacement of evaporative losses and moisture that leaves with the dewatered ash. Because of the poor separation of the buoyant fly ash, however, recycle systems are generally not suitable, where fly ash is sluiced to the same dewatering point as bottom ash. Chemical coagulants and flocculants are useful in the treatment of ash transport waters, to reduce suspended solids to acceptable levels for recycle or final discharge.

Flue Gas Desulfurization

Most coal-burning power plants use flue gas desulfurization (FGD) systems to control sulfur dioxide (SO_2) emissions. Water from various sources (e.g., clarified surface waters, cooling tower blowdown, and reclaim water) is used as makeup to wet FGD scrubber systems. Wet, calcium-based processes, those that use limestone ($CaCO_3$) or lime (CaO) as the alkaline reagent are the most commonly used FGD processes in utility applications. In these processes, SO_2 absorbed from the flue gas reacts with the alkaline species in the scrubbing liquor to form relatively insoluble calcium sulfite and calcium sulfate solids. These solids are concentrated in a clarifier-thickener or hydroclone separator and continuously removed from the system as a sludge requiring disposal. Throwaway disposal methods include pumping the sludge to ponds or dewatering the sludge, fixing it with fly ash and lime, and landfilling. Alternatively, byproduct gypsum may be produced for use as a raw material in the production of wallboard. To produce byproduct gypsum, a forced oxidation FGD process is used, wherein excess air is injected into the wet scrubber to oxidize sulfites to sulfate, which combines with calcium to yield gypsum [i.e., calcium sulfate dihydrate ($CaSO_4 \cdot 2H_2O$)]. Figure 33.28 depicts a wet limestone forced oxidation FGD process utilized by many power plants today.

The FGD process will typically employ a blowdown or wastewater purge stream to limit the buildup of chlorides and inert fines in

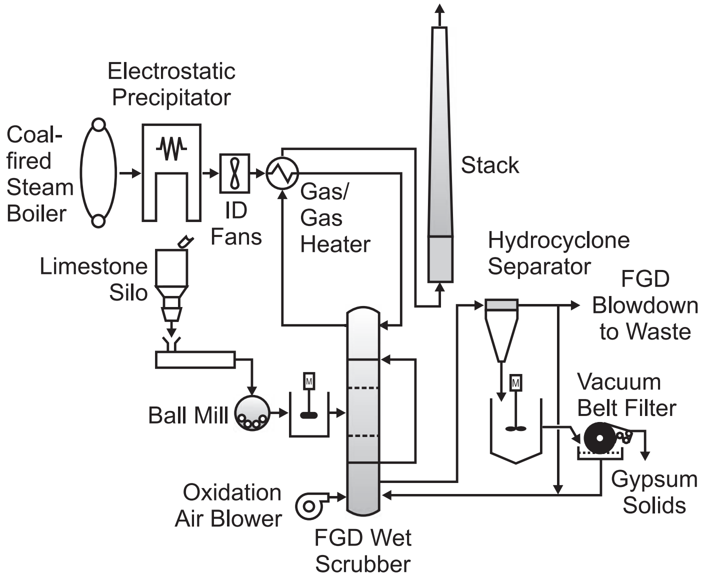

Figure 33.28 Simplified FGD system.

the scrubber system. FGD wastewaters are typically acid, highly saline solutions with variable quantities of suspended solids, metals, chlorides, fluorides, etc. FGD wastewater treatments employ a chemical/physical treatment process that includes a gypsum desaturation step using lime for pH adjustment, heavy metal removal with an organosulfide, coagulation with an iron salt such as ferric chloride, and flocculant addition in a secondary clarification step.

Wastewater and Discharge

Steam-electric power plants are subject to national, state/province, and local water pollution control regulations. Where these regulatory bodies differ on specific limitations for a given pollutant, the more stringent regulations generally apply. Some state/province and local regulations limit certain pollutants not limited by national guidelines.

A simplified tabulation of steam-electric plant wastewaters and their contaminant characteristics, by source categories, is shown in Table 33.5.

Source	Principal Contamination
Ash sluicing system	TSS*, TDS†, heat, oil
Low volume wastes‡	TSS, TDS, pH, oil
Metal cleaning wastes§	TSS, TDS, pH, iron, copper, other metals, oil
Boiler blowdown	TSS, iron, copper, oil
Main condensers, once-through cooling	Heat, residual chlorine
Main condensers, recirculating water blowdown	Residual chlorine, Zn, Cr, P, other cooling water additives
Area runoff¶	TSS, TDS, pH, oil
Intake water traveling screens and strainers	Solids (debris)
FGD systems and scrubbers	Solids (gypsum, sludge), TSS, TDS, pH, heavy metals

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*TSS, total suspended solids.

†TDS, total dissolved solids.

‡Low volume wastes, including wastes from ion exchange system regeneration, evaporator blowdown, flue gas wet scrubbers, floor drainage, cooling tower basin cleaning, and blowdown from recirculating service water systems.

§Metal cleaning wastes, including waterborne wastes from boiler tube cleaning, and boiler fireside cleaning, air preheater cleaning

¶Area runoff, including rainfall runoff from storage of coal, ash, and other materials.

Table 33.5 Major Wastewater Sources and Contaminants from Fossil-Fuel Steam-Electric Generating Plants

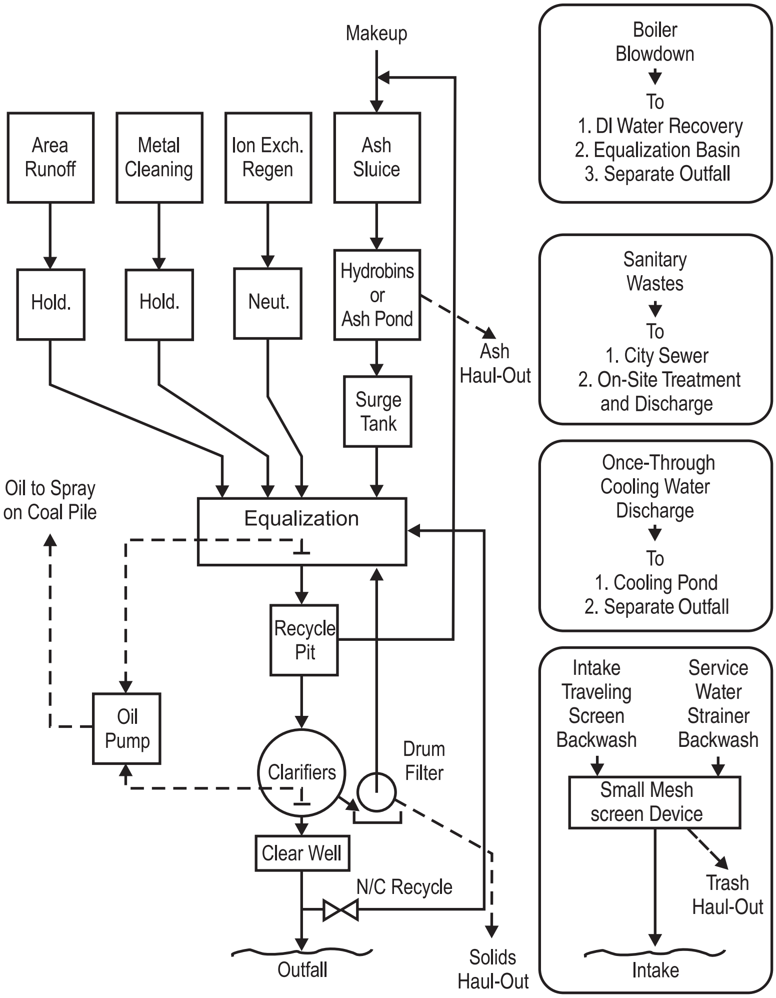

FIGURE 33.29 Water reuse and effluent treatment scheme for a coal-fired steam-electric plant.

Principles of water recycle, reuse, and effluent treatment for steam-electric plants are generally the same as for other process industries. Figure 33.29 illustrates one reuse and effluent treatment scheme for a coal-fired plant. In this illustration, bottom ash transport water is recycled. Fly ash is separately handled in a dry system. One of the difficult problems is proper handling of coal pile runoff without interfering with coal handling procedures in the large area used for coal inventory. The runoff is often high in heavy metals, alumina, and suspended solids, and may require recycle or direct treatment (Table 33.6).

Parameter	Concentration, mg/L
Total solids	1500–45 000
TDS	700–44 000
Total suspended solids	20–3300
Total hardness ($CaCO_3$)	130–1850
Alkalinity ($CaCO_3$)	15–80
Acidity ($CaCO_3$)	10–27 800
Manganese	90–180
Copper	1.6–3.9
Sodium	160–1260
Zinc	6.0–23.0
Aluminum	825–1200
Sulfate	130–20 000
Phosphorus	0.2–1.2
Iron	0.4–2.0
Chloride	20–480
Nitrate	0.3–2.3
Ammonia	0.4–1.8
BOD	3–10
COD	100–1000
Turbidity (JTU)	6–605
pH	2.8–7.8

Source: Development Document for Proposed Effluent Limitations Guidelines and New Source Performance Standards for Steam Electric Power Plants, EPA 440-1-73/029, March 1974.

Table 33.6 Typical Characteristics of Coal Pile Runoff

The segregation of dissimilar wastes is of special importance for nuclear power plants. High-purity (low-conductivity) wastewaters are kept separate from low-purity (higher conductivity) waters to facilitate reclamation and recycle of the high-purity waters. Chemical wastes, including ion exchange regenerants and chemical cleaning wastes, should be segregated from detergent wastes, because of their differing requirements for final treatment before discharge or reuse.

CHAPTER 34

The Oil Field Industry

Oilfield waters can vary a great deal from reservoir to reservoir. The produced water (PW) can have a wide variety of contaminants that vary in severity. The technology today is focused on mitigating both corrosion and scale, and helping with water clarification so that the water can be recycled or reused. Water will continue to play an important role in the future of the oilfield, as this resource continues to be scarce. Many technologies exist today that can help turn oilfield brine into water that can be returned to the environment.

Theory of Oil Formation

The organic theory, which is the most generally accepted hypothesis for the origin of oil, presumes that microscopic plant and animal life from the sea and tidal areas provided oil's raw materials (hydrogen and carbon). According to this theory, rivers transported great volumes of mud, sand, and products of surface erosion to the sea floor for millions of years, which were spread by tides and currents. Under the increasing weight of this accumulating debris, the ocean floors slowly sank and were compressed to form the sedimentary rocks that contain petroleum—sandstone, shale, porous limestone, and dolomite (a mixture of calcium and magnesium carbonates).

The organic components of trapped microscopic organisms were changed over time to petroleum, through chemical, physical, and biological influences (Fig. 34.1).

A less prevalent theory proposes that methane and possibly other related hydrocarbons originate in the earth's mantle and work their way to faults and traps in the crust. This theory has gained support because of recent findings of hydrocarbons in meteorites and in the more distant planets.

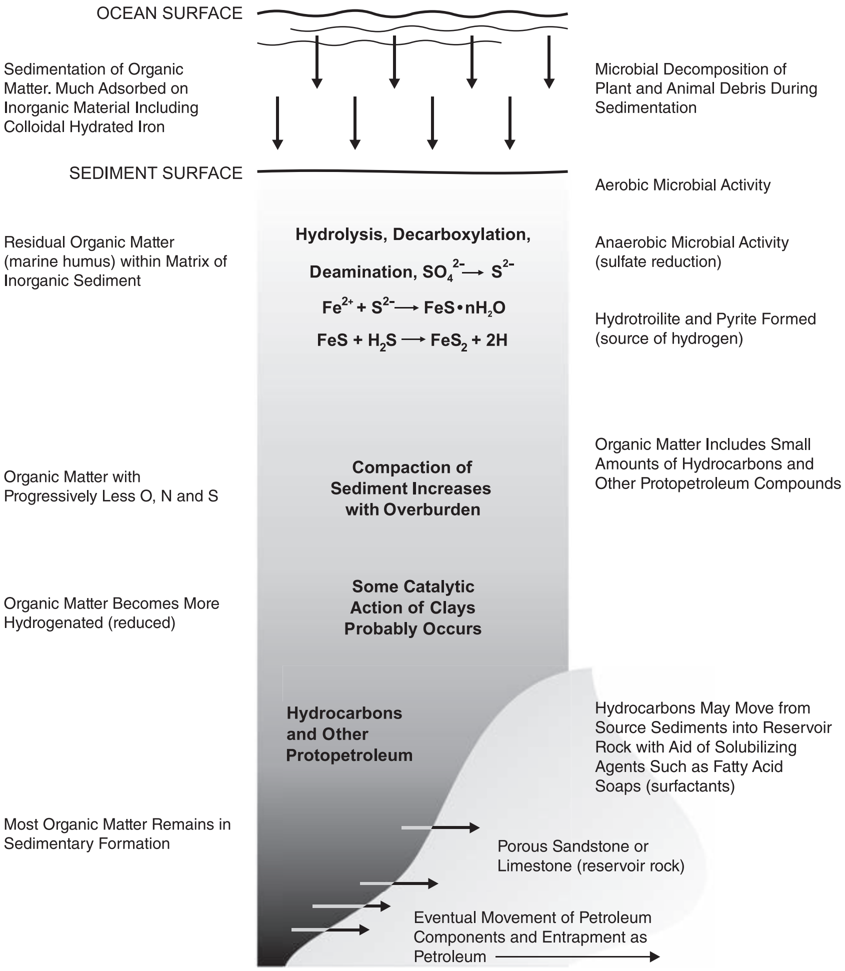

FIGURE 34.1 Events in the formation of petroleum from organic debris. (*Adapted from Davis, J. B., Petroleum Microbiology, Elsevier, Amsterdam, 1967.*)

A Few Basics about Petroleum

Naturally occurring petroleum is complex and variable in chemical composition. Its color ranges from light greenish brown to black. It may be fluid or so viscous as to be nearly solid. Although most people are familiar with the terms petroleum and crude, they may not quickly recognize the specific industry terms used to describe oils such as "conventional or unconventional oils, heavy oil and bitumen." In general, oil is called unconventional when it cannot be recovered by the conventional means of simply drilling a well. Unconventional

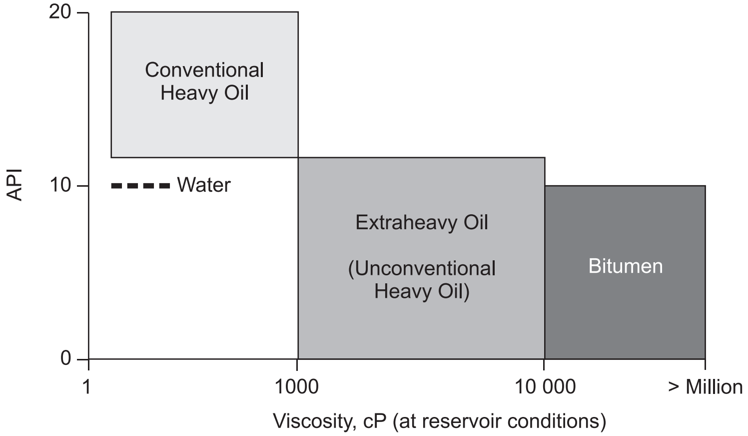

FIGURE 34.2 Definition of heavy oil and bitumen.[1]

oils are recovered by a variety of methods including surface mining, water flooding, steam stimulation or assistance, solvent extraction, gas injection, and others.

Crudes are commonly identified by American Petroleum Institute (API) gravity, a number that is inversely related to specific gravity (SG).

$$\text{API gravity} = (141.5/\text{SG}) - 131.5 \qquad (34.1)$$

API gravity can be confusing to those unfamiliar with petroleum terminology. In the oil industry, a high-gravity crude is rich in volatile materials and has a low SG (0.75–0.84), so the API gravity is in the range of 35 to 55°. Some heavy crudes have a SG close to that of water, and the API gravity may be as low as 15° at the standard temperature of 60°F (15.6°C).

Figure 34.2 provides a graphical definition for heavy oil and bitumen relative to API gravity and viscosity. Crude bitumen is a thick, sticky form of crude oil that is so heavy and viscous it will not flow unless heated or diluted with lighter hydrocarbons.

Accumulations of Petroleum

Petroleum is found only in porous sedimentary rock. It migrates horizontally and vertically, reaching a local structure or trap having a caprock seal, which contains the oil and creates the reservoir. In some

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[1] Banerjee, D.K., Oil Sands, Heavy Oil, and Bitumen: From Recovery to Refinery, PenWell Corp., 2012.

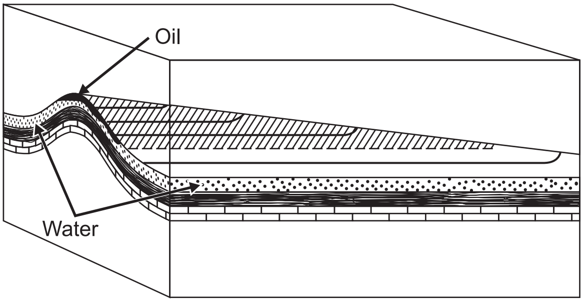

Figure 34.3 The separation of water and oil in an anticline, a folded structure topped by an impervious hood. (*Courtesy of API, from Primer of Oil and Gas Production*.)

instances, the oil ends up incorporated within shale or near the surface incorporated within loose sand or a partially consolidated sandstone mixture of sand, clay, water, and bitumen.

Many different shapes, sizes, and types of geologic structures form oil reservoirs. These include domes and anticlines, fault traps, unconformities, dome and plug traps, lens-type traps, and combination traps. An anticline type of folded structure is shown in Fig. 34.3, and a trap resulting from faulting is shown in Fig. 34.4.

The length and width of a reservoir can vary from one to several miles (kilometers), and the depth from a few feet (meters) to

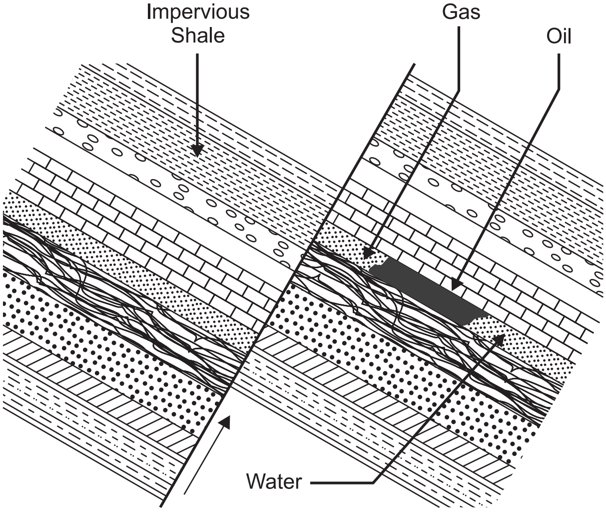

Figure 34.4 The separation of water and oil in sections of a fault, the displacement of layers along a slip plane. (*Courtesy of API, from Primer of Oil and Gas Production*.)

several hundred. A 1 acre (4000 m^2) reservoir with a depth of 10 ft (3 m) would contain 10 acre · ft, a common U.S. unit of measure. To estimate its petroleum content, the total pore volume (porosity) and percentage oil saturation (10–99%) must be known. The remaining fluid is interstitial (or connate) water. The U.S. standard measurement of volume in the petroleum industry is the barrel (42 gal, 5.6 ft^3, 0.16 m^3).

A 10 acre · ft reservoir contains 435 600 ft^3 (12 300 m^3). With a porosity of 20% and an oil saturation of 80%, the reservoir would contain:

U.S. Units: (435 600 ft^3)(0.2)(0.8) =70 000 ft^3 or 12 000 barrels of oil

Metric Units: (12 300 m^3)(0.2)(0.8) = 2000 m^3

Oil Sands and Heavy Oil Reserves

Major oil sands and heavy oil reserves are found extensively in the Athabasca deposits of Alberta, Canada, and in Venezuela along the Orinoco River. Numerous other counties including Kazakhstan, Russia, and the United States hold oil sands deposits which are orders of magnitude smaller in size.

In the late 1940s, Sidney Ellis and Karl Clark developed processes to enable valuable oil to be extracted from oil sands. Pilot plant operations initiated in the 1950s led to commercial scale construction of a synthetic oil facility in the Athabasca region in 1965 by Great Canadian Oil Sands, Ltd. The plant went into operation in 1968. Syncrude Canada, Ltd., began operating a commercial facility in 1978. Synthetic oil production from oil sand processing in Canada has developed into the largest industry of its type in the world.

Petroleum Production

When the drill penetrates the reservoir, oil, and gas are forced to the surface by natural reservoir pressure. The period during which oil is produced by natural reservoir pressure is referred to as primary production and is typically a period of a few months or several years.

The flowing well is constructed of “strings” of concentric vertical pipes called casings and a smaller pipe, usually 2 to 3 inches (51–76 mm) in diameter, called tubing, through which produced fluid flows. The largest diameter casing (the surface string) extends to a depth of 200 to 1500 ft (61–460 m); the intermediate string may reach a depth of 5000 ft (1500 m); a third casing (the oil string) may reach the producing zone. Some producing zones are at depths of 20 000 ft (6100 m) or more. The tubing into the producing formation is secured by a packer, which seals the space between the tubing and the final casing (Fig. 34.5). Occasionally, intermediate level strings

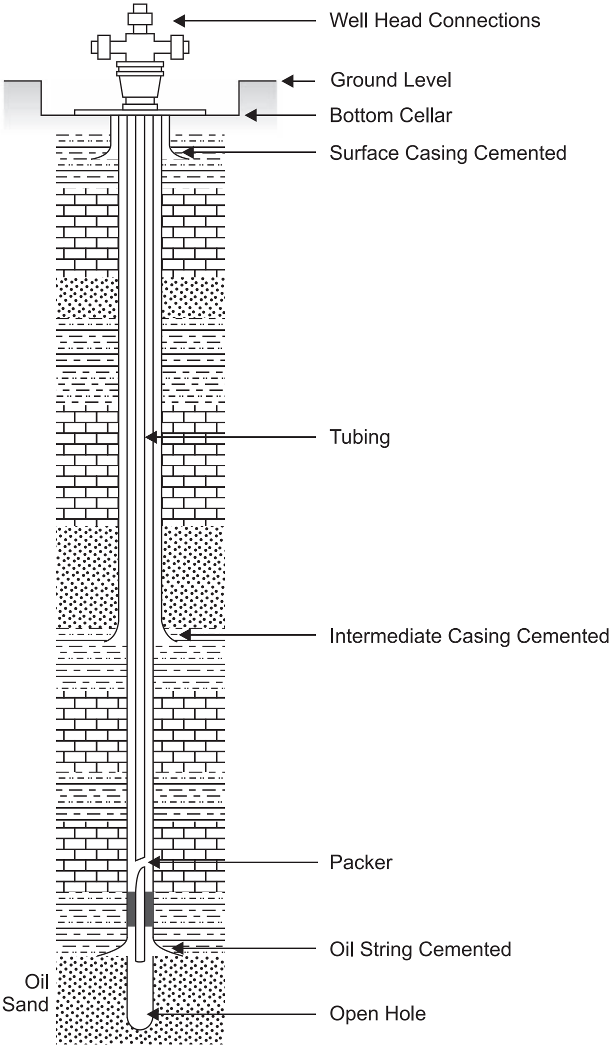

Figure 34.5 Typical arrangement of casing, string, and tubing in an oil well. (*Courtesy of API, from Primer of Oil and Gas Production*.)

are perforated, allowing production to flow simultaneously from shallower producing zones. A series of valves and flanges at the wellhead (called a Christmas tree) includes a small orifice plate (called a choke) to control flow.

Oil Dehydration

Oil leaving the producing well is a mixture of liquid petroleum, natural gas, and formation water (Fig. 34.6). During early primary production, water may be insignificant. Most production, however,

FIGURE 34.6 Oil is almost always produced as an emulsion, very different in appearance from finished oil products.

contains sizable proportions of PW (up to 90%). This must be separated from the oil, since pipeline specifications stipulate maximum water content (as low as 1% but up to 3 to 4% in some locations).

The initial separation vessel in a modern treating plant is called a free water knockout (FWKO) drum (Fig. 34.7). Free water, defined as that which separates within 5 minutes, is drawn off to a holding tank, to be clarified before reinjection or discharge. The remaining oil usually contains emulsified water and must be further processed to break the emulsion, usually assisted by heat, electric energy, or both.

Heater treaters (Fig. 34.8) are vertical or horizontal vessels in which the water-in-oil emulsion is resolved, invariably with the assistance of

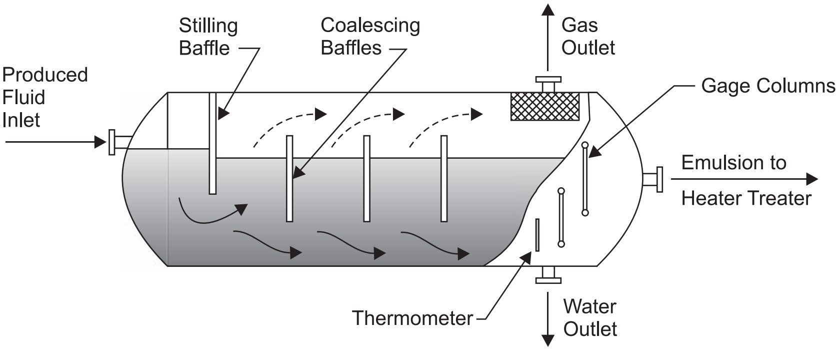

FIGURE 34.7 Free water and gas are separated from the produced fluid in this gravity separation vessel, simplifying emulsion breaking. (*Courtesy of API from Treating Oilfield Emulsions*.)

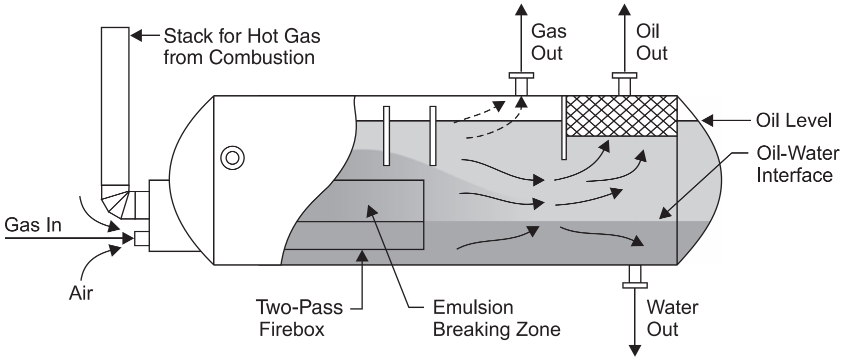

Figure 34.8 This heater treater uses the heat of combustion of gas or oil to heat the emulsion from the free water knockout drum, assisting chemical treatment to yield an oil of minimum water content. (*Courtesy of API from Treating Oilfield Emulsions*.)

emulsion breaking chemicals. The electrostatic treater employs heat, but also uses high-voltage alternating current to charge the water droplets, accelerating the process of coalescing smaller droplets into larger ones. The demulsified crude oil flows to a stock tank for pipeline shipment to a refinery.

Improved Recovery Techniques

In primary oil production, sufficient underground pressure exists to force the oil to the surface by natural mechanisms. As the well ages, its pressure naturally falls and at some point, introduction of artificial energy into the reservoir will be required to sustain production. This includes water flooding, gas injection, and other processing involving fluid or energy injection, whether for secondary or tertiary oil recovery.

Secondary recovery usually follows primary production, but may be conducted concurrently with it. Secondary recovery methods attempt to increase the degraded reservoir pressure by injecting water, natural gas, or other gases such as air or carbon dioxide. Waterflooding is the most common method of secondary recovery. A typical recovery factor from waterflood operations is about 30%.

Tertiary recovery is usually undertaken following secondary recovery, when production has dropped too low to justify continued operation. It is sometimes referred to as enhanced oil recovery (EOR). Tertiary methods attempt to increase the mobility of the oil in order to increase production. Tertiary techniques include thermal recovery (steam injection and in situ combustion), chemical injection or flooding, and carbon dioxide flooding. Steam injection is the leading form of both thermal recovery and EOR. Tertiary recovery techniques can add an additional 5 to 15% to the reservoir's total recovered production.

EOR techniques of some sort are usually required when the oil is heavy or extra-heavy (extremely low API gravity), is part of natural bitumen deposits (oil sands), or is extra viscous because of an extremely cold reservoir location (e.g., Alaskan north shore). Steam injection is the most commonly practiced EOR technique for extracting heavy, extra-heavy, and bitumen-based oil.

Waterflooding

As noted, waterflooding is the most common method of secondary recovery practiced in traditional oilfields. In waterflooding, water is injected as a uniform barrier through the producing formation from a series of injection wells toward the producing well. Such injection wells can either be converted producing wells or new wells drilled specifically for injection of flooding water.

Proper spacing of the injection wells is important. Most reservoirs are flooded through wells distributed uniformly throughout the reservoir, peripheral injectors may flood others.

The permeability of the reservoir rock has a great bearing on its suitability for waterflooding. Rock is considered permeable if a significant fluid flow will pass through it in a short time; it is impermeable if the rate of passage is negligible.

The unit of permeability is the *darcy*, standardized by the API as follows: "A porous medium has a permeability of one darcy when a single-phase fluid of one centipoise viscosity that completely fills the voids (or pores) of the medium will flow through it at a rate of one centimeter per second per square centimeter of cross-sectional area under a pressure or equivalent hydraulic gradient of one atmosphere (760 mm of Hg) per centimeter."

The permeability of formation cores is generally in the range of 5 to 1000 millidarcies (md) (1 md = 0.001 d). A rough practical example of 1 d would be 1 ft^3 (0.028 m^3) of sandstone passing approximately one barrel (0.16 m^3) of oil per day with a pressure drop of 1 psi (6.9 kPa).

Permeability and porosity vary greatly both laterally and vertically in the typical reservoir rock. A rock whose permeability is 5 md or less is called "tight sand" or a "dense limestone" according to its composition. The following are rough permeability ratings:

- 1 to 10 md (fair permeability)
- 10 to 100 md (good permeability)
- 100 to 1000 md (very good permeability)

It is imperative for efficient flooding that the water be compatible with the reservoir formation. A desirable water for this purpose is that produced from the formation, after separation from the oil and gas. However, the amount of water required for flooding far exceeds the volume produced, so supplemental water is needed.

PW and supplemental surface waters must be clarified to remove residual oil accumulations, sand, and dirt washed from the producing formation, oxidized inorganic or organic suspended solids (SS), and corrosion products. Quality required for waterflooding is dictated by the permeability restriction of the reservoir. Currently, the most popular equipment for clarification is the flotation cell employing gas diffusion to produce clear effluent.

Where injection water must include surface or well water of lower salinity than the original formation water, chemical incompatibility with the formation rock may result. This may cause swelling of clay in the rock, blockage of the reservoir pores, and loss of oil production. Historically, the suitability of injection water has been determined through analyses of the waters in question, membrane filtration, or laboratory work with formation cores. All of these procedures have the disadvantage that the waters have been removed from the actual reservoir environment and may have changed.

Most injection waters are passed through some type of filter, with the media and design depending on the reservoir permeability. The filters must clean the water and remove any impurities, such as shells and algae. Typical filtration is to 2 micrometers, but really depends on reservoir requirements. The filters are fine enough to remove potential impurities which would block the pores of the reservoir. Types of filters include mixed media beds, individual well cartridges, or septum filters using diatomaceous earth (DE) as a filter aid. In some cases, more sophisticated treatment such as clarification or lime softening may be needed.

Deaeration may be required to reduce corrosion or to prevent iron oxidation and growth of certain bacteria. This may be accomplished by a deoxygenation tower which is a form of degassifier—dry gas, typically air, is passed counter current to the filtered water as it splashes onto a series of trays. Oxygen is stripped into the gas stream by this process and exits out the unit through a vent. An alternative method of deoxygenation, which may actually be used in addition to deoxygenation towers, is to add an oxygen scavenging agent such as sodium or ammonium bisulfite

Polymers or surfactants may be added to aid waterflooding. Polymers function by thickening the water used in the waterflooding process, resulting in improved fluid-flow patterns. Surfactants lower the interfacial tension of oil, facilitating oil flow to the well.

Steam Injection/Thermal

Waterflooding is not effective for recovery of low API gravity oil from relatively shallow formations with reservoir temperatures below about 120°F (49°C). This situation responds, however, to steam injection. Steam injection is a form of tertiary recovery, specifically a form of thermal recovery. There are different forms of the technology, with the two main ones being cyclic steam stimulation (CSS) and steam flooding.

With CSS the well is taken out of service and steam is injected for a period of several weeks to heat the oil-bearing rock. Next, the well may be allowed to sit for days to weeks to allow heat to soak into the formation. Finally, the oil well is returned to service until stimulation may be required again. A single well is used throughout the process. This method is also known as the huff-and-puff method of steaming.

The most common method of steam injection, however, is steam flooding which may also be known as a steam drive. With this method, some wells are used as steam injection wells and other wells are used for oil production.

The steam used is generated by a once-through steam generator or once through heat recovery steam generator (HRSG) and may be either wet or dry. When wet steam is used, approximately 10 to 40% of the mass sent downhole is present as hot water. The water phase doesn't contain as much thermal energy as the steam phase, so this method requires more mass downhole than when dry steam is used. Steam is injected into one of a group of centrally located displacement wells, with the steam and hot water then radiating outward toward the peripheral oil wells served by each of the injection wells.

Dry steam is produced by putting the wet steam through a steam separator prior to sending it to the well.

A form of steam flooding that has become popular in the Alberta oil sands is steam assisted gravity drainage (SAGD), in which two horizontal wells are drilled, one a few meters above the other, and steam is injected into the upper one. The intent is to melt the bitumen and reduce its viscosity to the point where gravity will pull it down into the lower producing well.

As time passes at any steam-flood site, there is a gradual increase in temperature of the produced fluids to about 160 to 180°F (71–82°C). The wells produce 6 to 8 bbl of water per barrel of oil (1–1.3 m^3/m^3). The oil and water are separated in dehydration tanks using emulsion breakers, and the water must then be processed to render it suitable for feed to the steam generators or for disposal. The salinity and chemical characteristics of the PW vary greatly from one site to another. Table 34.1 includes the analysis of several PWs after the dehydration tanks.

Figure 34.9 shows a typical flow diagram of a water treatment plant servicing a steam flooding facility. After dehydration, oil is removed in dispersed gas flotation units, assisted by cationic emulsion breakers. The skimmings are recovered, and treated water is discharged to storage. The flotation unit and storage tanks are gas blanketed to avoid pickup of oxygen. An oxygen scavenger is usually applied at this point. If the Stiff-Davis Index is strongly scaling, a stabilizing inhibitor is applied here to prevent problems with calcium carbonate scale formation. Gypsum (calcium sulfate) may also be a problem. The water is then polished through septum filters. A variety

State	County	Formation	Constituents, mg/L							
			Na	Ca	Mg	Cl	SO_4	SiO_2	HCO_3	TDS*
Oklahoma	Kingfisher	Oswego	56 250	8300	260	98 300	180		50	166 652
Kansas	Ellis	Arbuckle	16 800	2630	690	30 500	2880		315	54 072
New Mexico	Lea	San Andreas	9150	1500	500	17 800	2000		1000	32 329
Texas	Hopkins	Paluxy	5640	630	40	8350	120		500	15 417
California	Kern		3936	124	66	5800	216		73	10 159
California	Kern		6725	235	115	10 714	216		52	18 382
California	Kern (Kern River)		184	25	5	170	65		234	620
Alberta	Cold Lake		800	5.3	< 1.6	1200	29	200	370	2620
Alberta	Fort McMurray		2500	50	< 4.2	4100	< 10	110	190	6900
Saskatchewan	Lloydminster		3400	140	52	5100	55	180	144	10 200
Saskatchewan	Lloydminster		1800	110	13	3000	22	150	380	6400

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*Total dissolved solids.

Table 34.1 Analyses of Several PWs

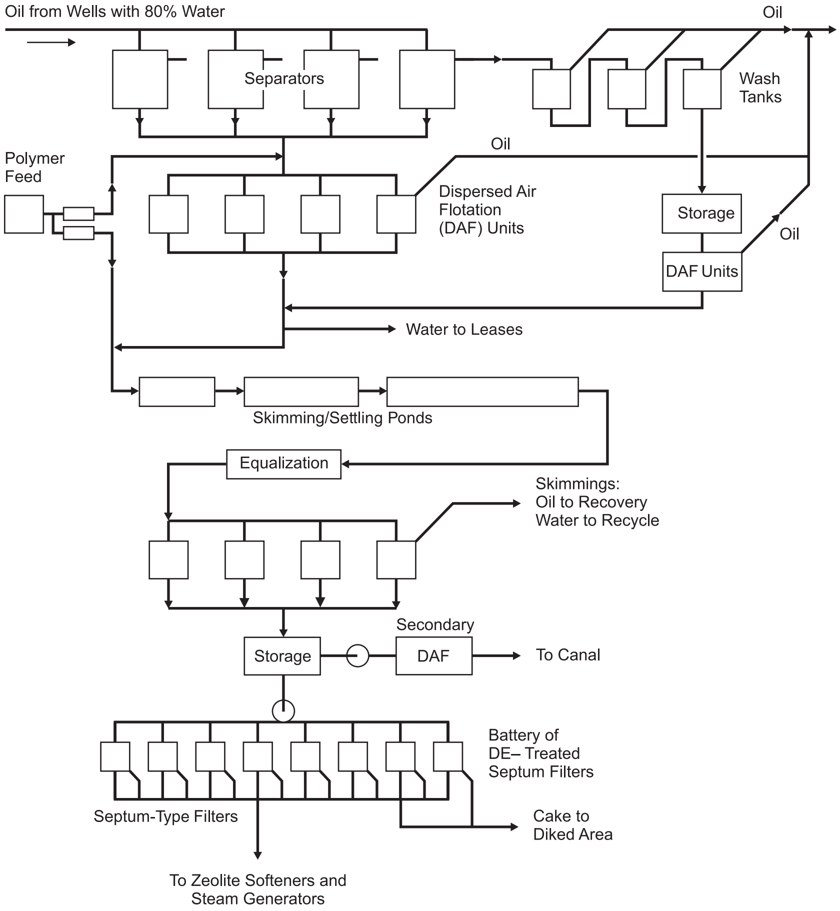


Figure 34.9 Treatment of PW for steam flooding.

of filter aids can be used, including specially processed cellulose, DE, and vermiculite. The filter is first precoated by recirculation; then it is put on stream, with a continuous application of filter aid (body feed) of 2 to 3 mg/L per mg/L oil.

The filtered water is then softened through sodium zeolite ion exchange softeners (Fig. 34.10). The high salinity of the PW makes softening difficult, so almost universally, a polishing softener follows the primary unit to assure low hardness in the finished water. The softened water is then sent to the various steam generators in different areas of the oilfield, sometimes several miles away. Alternatively, filtered water may be softened using warm or hot lime softening followed by sodium zeolite softening.

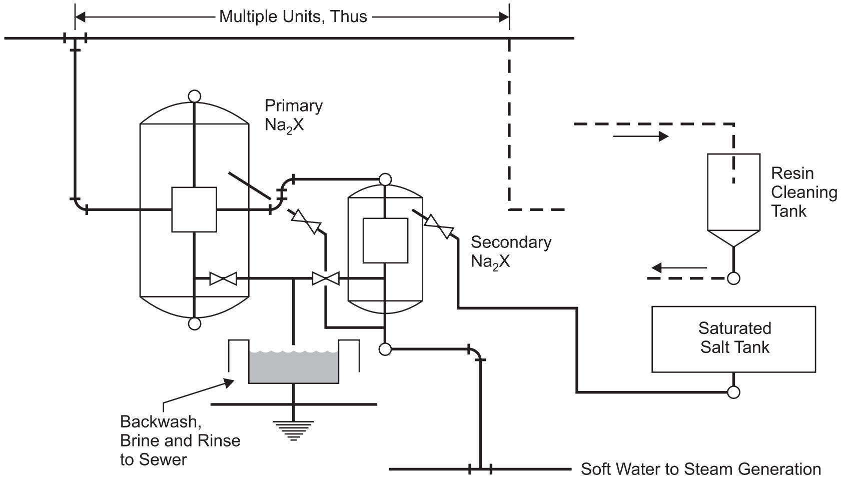


FIGURE 34.10 Two-stage sodium softening of de-oiled, filtered, produced PW to render it suitable for high-pressure boilers.

The typical steam generator is unusual in that it is a once-through unit (Fig. 34.11). Feedwater is preheated to avoid acid deposit attack of the economizer, and then flows through the economizer to recover heat from the stack gas. The feedwater then passes through the radiant and convection sections of the steam generator, where steam is generated. However, unlike conventional drum-type boilers, the fluid leaving the generator has a quality from 65 to 90% (commonly 75–80%); for example, at 80% quality the fluid contains 80% steam

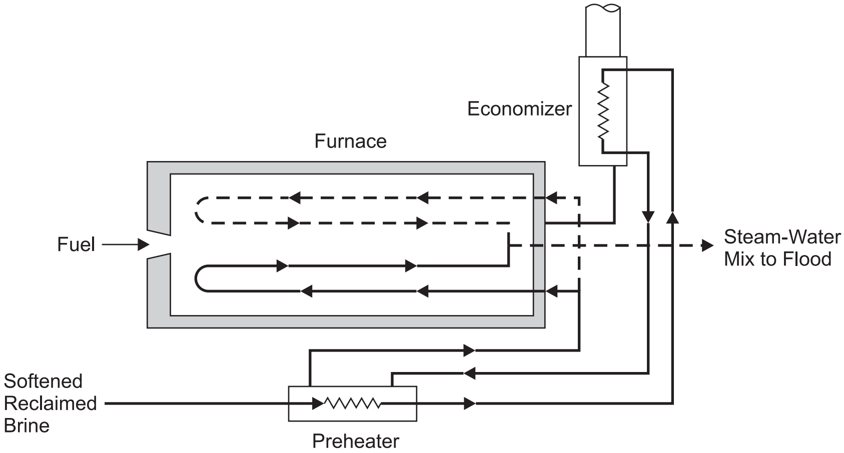


FIGURE 34.11 Once-through high-pressure steam generator designed for steam flooding and recovery of the low API gravity viscous oils of Lower California.

and 20% water by weight. Because the steam specific volume at 900 psig (6.2 MPag) is 0.49 ft^3/lb (0.031 m^3/kg), while the specific volume of water is only 0.021 ft^3/lb (0.0013 m^3/kg), the discharged fluid contains 99% steam and only 1% water by volume.

The water in the discharged steam contains all of the solids present in the feedwater. At 80% quality, 5 lb (2.3 kg) of feedwater produces 4 lb (1.8 kg) of steam and 1 lb (0.45 kg) of water, so the solids have been concentrated 5 times. The relationship between steam quality and concentration is:

$$\text{Concentration Ratio (CR)} = 100 - \text{quality} \tag{34.2}$$

Even though these waters are softened, chemically deaerated, and treated, it is still surprising that such high-salinity waters could be suitable feedwater for steam generators that frequently operate at pressures over 1000 psig (6.9 MPag). High fluid velocity and low heat flux relative to traditional boiler designs have been identified as the main reasons why more scale doesn't form in the once-through steam generators commonly used for steam injection.

In recent years, once-through HRSGs, traditional boilers, and hybrid boilers have also been used to generate steam for steam injection. Traditional and hybrid boilers require a better-quality feedwater and typically operate using evaporator distillate.

Depending on the depth of the injection well, and the permeability of the formation, the steam generators may operate at a pressure as low as 300 psig (2.1 MPag) and as high as 1500 psig (10.3 MPag). This pressure is maintained by the boiler feed pumps.

Chemical Flooding

Chemical injection uses dilute solutions of various chemicals to aid mobility and reduce surface tension of the oil. Injection of alkaline or caustic solutions into reservoirs that have naturally occurring organic acids in the oil may lower the interfacial tension enough to increase production. Injection of a dilute solution of a water-soluble polymer to increase the viscosity of the injected water can also increase the amount of oil recovered in some formations. Dilute solutions of surfactants may be injected to lower the interfacial tension or capillary pressure that impedes oil droplets from moving through a reservoir. Use of these methods is usually limited by the cost of the chemical program. Chemicals are commonly injected in separate batches or slugs into several wells and production occurs in other nearby wells.

Underground Combustion

The process of recovering bitumen by underground combustion is accomplished by drilling two wells into the oil sand deposit, one for injection and one for recovery. Bitumen at the base of one of the wells is ignited. Injected air feeds the combustion process and moves it through the reservoir as temperatures of 660 to 840°F (350–450°C) are attained. The bitumen is thermally cracked and vaporized. The cracked oils, gases, and vapors are driven toward the production well by injected air and collected.

Hydraulic Fracturing

Hydraulic fracturing is a recovery technique in which rock is fractured by a pressurized liquid. It may also be known as fraccing, fracking, hydrofracturing, or hydrofracking. The process involves the high-pressure injection of fluid into the well to create cracks in the deep-rock formations through which natural gas, petroleum, and brine can flow more freely. Such treatment is generally necessary to achieve adequate flow rates in shale gas, tight gas, tight oil, and coal seam gas wells. Some hydraulic fractures can form naturally in certain veins or dikes.

The injection fluid is typically water containing small grains of sand, aluminum oxide, ceramics, or other small particulates used in hydraulic fracturing, called proppants, suspended with the aid of thickening agents. When the hydraulic pressure is removed from the well, these small particulates hold the fractures open. Hydraulic fracturing is highly controversial in many countries.

Oil Shale

Extracting oil from oil shale requires conversion of solid hydrocarbons found in the rock to liquid form, so that they can be pumped or processed. This is done by heating the rock to a high temperature, and separating and collecting of the resultant liquid. This heating process is also known as retorting. Oil shale processing may be done in one of two ways: surface retorting and in-situ retorting.

Surface Retorting

The processing of oil shale by surface retorting involves large-scale mining operations, since the amount of oil in economically treatable shale is usually only 10 to 15% of weight of the native shale. At 15%, the production of 100 000 barrels (16 000 m^3) of oil would produce a residue of about 100 000 tons (91 000 tonne) of spent shale.

The release of oil is accomplished by heating the raw shale in a device like a kiln, although there is hope that in situ retorting may prove practical in the future.

Since the heat capacity of the shale is high, this process consumes a great deal of energy, which is one reason for its rather slow development. The hydrocarbons released from the shale may be processed by fractionation and extraction, to yield light ends and heavy fractions that may be used as refinery feedstock or fuel for retorting and steam generation.

Wastewater problems are similar to those of the refineries and coal-fired utility stations, the major one being the runoff from the large volumes of spent shale residue.

In-Situ Retorting

In-situ retorting processes oil shale underground. This eliminates the problems of mining, handling, and disposing of large quantities of material, which occurs for above ground retorting. With in-situ processing, the oil shale is slowly heated underground and the resulting liquids and gas extracted directly from the reservoir much like crude oil. Various technologies differ by the method used to introduce heat underground, but follow the same basic principle.

Bitumen Recovery from Surface Mining

Raw oil sand is collected in open pit mines using massive bucket wheel excavators and electric draglines. To obtain one barrel (0.16 m^3) of recoverable, synthetic crude oil from oil sand, about 1.6 tons (1.5 tonne) of oil sand must be mined and processed. It is estimated that 10% of the energy obtained from the final synthetic crude is required for oil sand mining. Once mined, methods such as hot water extraction, cold-water extraction, solvent extraction, direct coking, and fluid coking are employed to recover the oil sand hydrocarbon for fuel processing.

Hot Water Processing

Hot water processing requires mixing the sand with water at a temperature of about 195°F (90°C), to form a pulp containing 60 to 85% solids. Sodium hydroxide (NaOH) and other conditioners can be added to control pH and aid in separation. Conditioning is carried out in a rotating, steam-heated drum. Large quantities of water are added, and the layers disintegrate. The conditioned pulp is pumped to separation cells, where the sand settles and the bitumen oil froths to the surface on the rising bubbles. The sand is separated, and the bitumen oil mixture is collected for further processing.

Direct Coking

Direct coking is a pyrolysis process utilizing a fluidized bed reactor to distill and remove bitumen from the oil sand matrix. Oil sand is heated in a coker to about 900°F (482°C). At this temperature, the volatile synthetic oil separates from the sand matrix and is recovered from the coker as a condensed liquid. Coke deposits form on the sand as a result of thermal cracking of bitumen. The coke bearing sand is then fluidized with air and transferred to a burner operating at 1400°F (760°C) to drive coke from the sand, producing flue gas, and hot clean sand. A portion of this sand supplies heat for additional coking.

Upgrading Bitumen and Heavy Oil to Produce Synthetic Fuels

Heavy and extra-heavy crude oils and crude bitumen are viscous semisolid forms of oil that do not easily flow at normal temperatures. They must be upgraded to lighter synthetic crude oil, blended with diluents to form dilbit, or heated to reduce their viscosity in order to flow through oil pipelines.

In the Canadian oil sands, bitumen produced by surface mining is generally upgraded onsite and delivered as synthetic crude oil. Upgrading may involve multiple processes including vacuum distillation, de-asphalting, cracking, and hydrotreating.

In-situ producers do not have the ability to upgrade their bitumen in the same manner. This bitumen is typically diluted to improve flow characteristics using either conventional light crude or a cocktail of natural gas liquids. The resulting diluted bitumen, or dilbit, has the consistency of conventional crude and can be pumped through pipelines to upgraders or refineries.

The Nature of Oilfield Waters

After establishing injection and feedwater quality requirements, steps must be taken to eliminate or control scaling, corrosion, and fouling of surface equipment, tanks, lines, and steam generators to prevent interruption of water or steam injection and a decrease in oil production.

It is necessary to conduct several types of analyses to identify and evaluate these potential problems. Analyses must be run at points throughout the water system, because changes through the system provide data for proper control. In waterflood systems, the job of injection system control starts at the producing well, for it is here that water begins to change. As water enters the production tubing, a pressure drop occurs that could cause precipitation, either in the tubing string or in the formation. As the produced fluid approaches the surface, further pressure drop causes loss of gases and a reduction in temperature. In steam injection systems, scaling, fouling, and corrosion can occur anywhere there is a significant change in water temperature, heat input, or concentration of the water by evaporation.

Substances in oilfield waters are classified as dissolved ionic solids, SS, dissolved gases, problem-causing bacteria, dissolved organic material, and residual oil.

Total Dissolved Solids

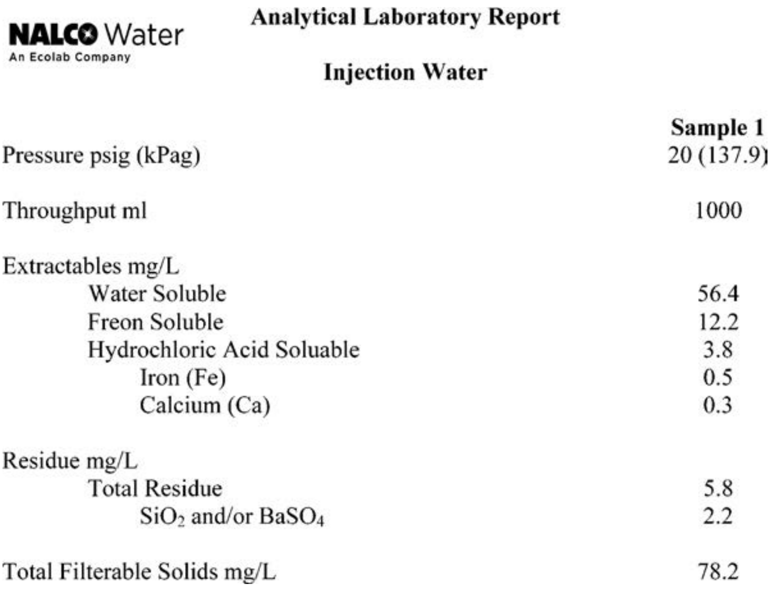
In oilfield brines, total dissolved solids (TDS) ranges from less than 10 g/L to over 350 g/L, of which sodium chloride (NaCl) constitutes 80% or more. Troublesome cations found in oilfield waters are calcium (Ca^{+2}), magnesium (Mg^{+2}), barium (Ba^{+2}), strontium (Sr^{+2}), ferrous iron (Fe^{+2}), and lithium (Li^{+}). Commonly encountered anions are chloride (Cl^-), sulfate (SO_4^{-2}), bicarbonate (HCO_3^-), bisilicate ($HSiO_3^-$), and sulfide (S^-).

Potassium (K^+), boron (B^{+3}), zinc (Zn^{+2}), and copper (Cu^{+2}) are also frequently measured. Soluble organic acids and ammonium (NH^{+1}) compounds can also be present at high concentrations. A few typical brine combinations were shown in Table 34.1.

Suspended Solids

Various inorganic and organic solids are found in petroleum waters. These may be particles of metal oxides from well casings or oxidized iron or manganese originally in the water. Other SS may be silt, sand, clay, or bacterial bodies. Lime softening solids, primarily calcium carbonate ($CaCO_3$) and magnesium hydroxide [$Mg(OH)_2$], from precipitated solids carryover are common in systems using lime softening.

SS particulates can be collected on a 0.45 μm membrane filter for identification. The filtered solids are analyzed separately (Fig. 34.12). A high concentration of solvent extractables usually indicates the need for better demulsification or clarification of the water. Hydrochloric acid soluble materials include carbonates of calcium, magnesium, and iron, as well as oxides and sulfides of iron. Residue remaining after treatment could include silica, barium sulfate, calcium sulfate, or heavy hydrocarbons such as asphaltenes, which are insoluble in most solvents. The residue could also include bacteria.



NALCO Water
An Ecolab Company

Analytical Laboratory Report

Injection Water

	Sample 1
Pressure psig (kPag)	20 (137.9)
Throughput ml	1000
Extractables mg/L	
Water Soluble	56.4
Freon Soluble	12.2
Hydrochloric Acid Soluable	3.8
Iron (Fe)	0.5
Calcium (Ca)	0.3
Residue mg/L	
Total Residue	5.8
SiO_2 and/or $BaSO_4$	2.2
Total Filterable Solids mg/L	78.2

Figure 34.12 Analysis of SS.

Dissolved Gases

The gases of greatest concern are hydrogen sulfide (H_2S), carbon dioxide (CO_2), and oxygen (O_2).

PWs containing hydrogen sulfide are called sour waters. Oil reservoirs can become sour through the activity of sulfate-reducing bacteria (SRB) in the producing formation. H_2S concentrations can reach several hundred milligrams per liter. H_2S can also be produced in the water handling system by the same bacteria. Any increase in H_2S concentration along the water system which is not caused by blending should be considered an indication of bacterial activity.

As H_2S is extremely poisonous, all sour oilfield operators post conspicuous signs at tanks or vessels, cautioning against inspection without the use of breathing equipment.

H_2S in contact with iron produces iron sulfide (FeS), which can accelerate corrosion and cause serious scale. The sulfides of most metals are insoluble in water. H_2S in contact with dissolved oxygen (DO) can produce elemental sulfur, also a potential foulant.

$$H_2S + \frac{1}{2}O_2 \rightarrow H_2O + S^0 \tag{34.3}$$

Carbon dioxide is an ionizable gas, forming carbonic acid (H_2CO_3) when dissolved in water at pH below 8.3. Although carbonic acid is a relatively weak acid, it is one of the greatest contributors to production well and waterflood system corrosion. Production well concentrations of CO_2 can exceed 200 mg/L, much of which is lost to the atmosphere when the produced fluids leave the well. Carbon dioxide is also responsible for dissolving limestone reservoir rock, increasing both hardness and alkalinity.

DO is rarely present in produced fluids coming from the reservoir, unless entrained through leakage, but it is perhaps the most serious corrodent participating in oilfield water corrosion mechanisms. Oxygen is a highly active element. Even in small amounts, it can cause serious corrosion in lines, heat exchangers, and steam-operated equipment. Corrosion increases with increasing oxygen content.

Problem-Causing Bacteria

Of several types of bacteria responsible for corrosion and formation of plugging type solids, the most serious offender is the anaerobic sulfate-reducing bacterium *Desulfovibrio desulfuricans*. SRB are bacteria that can convert sulfate to sulfide. The SRB are anaerobic bacteria and as such do not require free oxygen for their metabolism. Their presence in water systems is most problematic since these anaerobes are likely to reside in areas where oxygen depleted regions exist. Additionally, the product of sulfate reduction is hydrogen sulfide (H_2S), an undesirable corrosive species.

SRB can easily be determined with laboratory and field testing of fresh sample. Analysis takes a minimum of 48 hours for results and may not differentiate between multiple microorganisms present.

Residual Oil

Problems with oil water separation equipment and chemistry can lead to higher residual oil present in water stream. Residual oil contributes to fouling of heat exchangers, evaporators, and steam generators.

There are a great number of test methods and online monitors for various forms of oil in water which may or may not provide similar values. For a qualitative determination of residual oil, solvent extraction followed by weighing is recommended. This procedure requires time, limiting its use for monitoring.

Mineral Scales

The mineral scales of greatest concern to oil producers are calcium carbonate, calcium sulfate, and barium sulfate. Strontium sulfate, a less common scale, can also cause problems. Several iron compounds are of concern, related to corrosion or to oxidation of ferrous iron because of oxygen intrusion. Table 34.2 lists common scales with system variables that affect their occurrence.

Name	Chemical Formula	Primary Variables
Calcium carbonate (calcite)	$CaCO_3$	Partial pressure of CO_2, temperature, TDS
Calcium sulfate		
Gypsum (most common)	$CaSO_4 \cdot 2H_2O$	Temperature, pressure, TDS
Anhydrite	$CaSO_4$	
Barium sulfate	$BaSO_4$	Temperature, TDS
Strontium sulfate	$SrSO_4$	
Iron compounds		
Ferrous carbonate	$FeCO_3$	Corrosion, dissolved gases, pH
Ferrous sulfide	FeS	
Ferrous hydroxide	$Fe(OH)_2$	
Ferric hydroxide	$Fe(OH)_3$	
Ferric oxide	Fe_2O_3	

Table 34.2 Most Common Scales

Mineral scales can form in many areas:

- Supersaturation can occur in the formation face as the produced fluids enter the production tubing.
- Scale can form throughout the length of the production tubing, on sucker rods, and in downhole pumps.
- In the heater treater, scale can form in surface vessels and on the heating surfaces.
- In the water handling system, scale can form in injection water pumps, surface lines leading to injection wells, and rock surfaces in the injection formation.
- In the feedwater system for steam injection, scale can form at heat exchangers, evaporators, evaporator and radiant sections of the steam generator, and steam separator.

Mineral Scales in Water Injection Systems

Calcium Carbonate

Calcium carbonate equilibria are frequently upset in oilfield waters, due to changes in temperature, pressure, and pH. Since calcium carbonate solubility decreases with increasing temperature, injection from the surface to a warm formation increases the chance of calcium carbonate deposition. Its solubility increases as the TDS content increases. For instance, the addition of 200 g/L NaCl increases $CaCO_3$ solubility by over 100%. Prediction of calcium carbonate scale potential has been the subject of much research. The Langelier Saturation Index (LSI) attempted to relate calcium and alkalinity concentrations to pH, temperature, and TDS. However, this had limited value in oilfield brines.

The Stiff–Davis Index is now widely accepted for predicting calcium carbonate deposition in oilfield systems. To be useful, the analytical data must be determined on freshly drawn samples; analyses determined in a laboratory are not reliable, since the character of the water may change substantially. The Stiff–Davis Index ranges from –2.0 to +2.0. Positive numbers indicate a progressively severe supersaturation; negative numbers indicate an under saturated solution. The validity of the index depends on the accuracy of the analysis.

Calcium Sulfate

Most calcium sulfate deposits found in the oilfield are gypsum ($CaSO_4 \cdot 2H_2O$), the predominant form at temperatures below 100°F (38°C); above this temperature, anhydrite ($CaSO_4$) may be found. Gypsum solubility increases with temperature up to about 100°F (38°C), and then decreases with increasing temperature. Sodium chloride increases the solubility of anhydrite, as it does for calcium

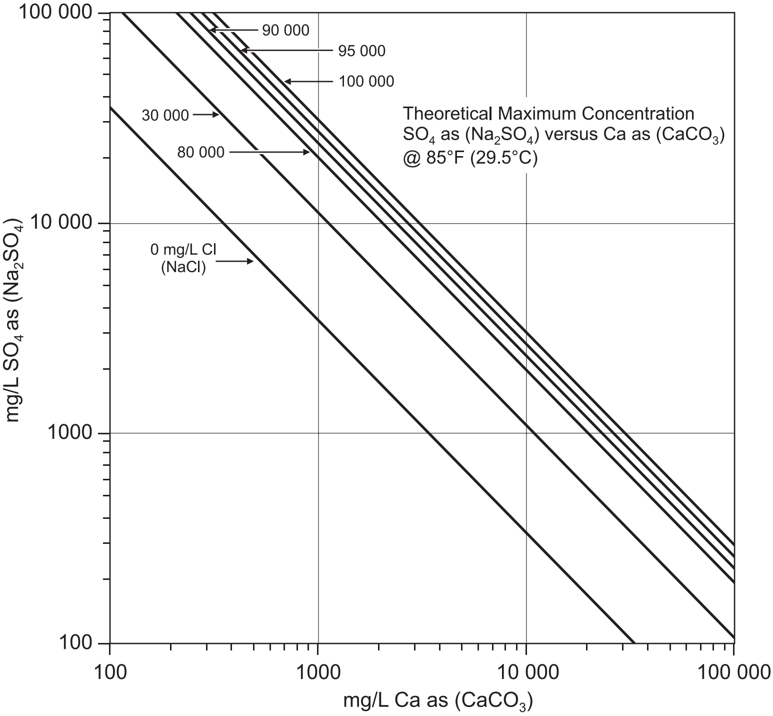


FIGURE 34.13 Calcium sulfate solubility at various brine levels.

carbonate, up to a salt concentration of approximately 150 g/L. Higher salt concentrations decrease calcium sulfate solubility. The addition of 150 g/L NaCl to distilled water triples the solubility of gypsum.

One of the more recent predictive indexes for gypsum are that developed by Skillman, McDonald, and Stiff. Calcium sulfate precipitation usually results from the mixing of two waters, one of which has a high calcium or sulfate concentration. A solubility graph relating calcium and sulfate concentration to total brine concentration is shown in Fig. 34.13.

Barium Sulfate

Barium sulfate solubility is the lowest of the usual scales, approximately 2.3 mg/L in distilled water. Increasing salt concentration increases the solubility of barium sulfate. The addition of 100 g/L NaCl to distilled water, increases the solubility of barium sulfate from 2.3 mg/L to approximately 30 mg/L at 77°F (25°C).

The solubility of barium sulfate increases with temperature. The combined effect of temperature and sodium chloride concentration can increase solubility to approximately 65 mg/L at 203°F (95°C).

Barium sulfate deposition usually results from the mixing of barium-rich water with sulfate-rich water. Such a combination should be avoided, but where mixing is unavoidable, chemical inhibitors may control deposits.

Scale Removal and Prevention

Most scales are typically removed by some form of mechanical cleaning, but can also be removed by chemical cleaning. Scales such as barium sulfate, which cannot be removed chemically, may require replacement of surface lines or abandonment of the well.

The first scale inhibitors were the inorganic polyphosphates, but their limitations were quickly discovered. Above 140°F (60°C), they revert to orthophosphate, as they do at acidic pH or over a long residence time. The orthophosphate form does not inhibit scale. Present day oilfield scale inhibitors are of three types:

1. Esters of polyphosphoric acid
2. Phosphonates
3. Organic polymers, such as polymers or copolymers of acrylic or methacrylic acid

The phosphate ester formulations are versatile for most oilfield water applications. Phosphonates and polymer products have definite advantages where water temperatures exceed 200°F (93°C). Dosages vary with temperature and the concentration of SS, since solids adsorb the inhibitor, requiring higher concentrations for effective inhibition. Dosage is directly proportional to the degree of supersaturation.

When applying scale inhibitors to producing wells, the "squeeze" technique is frequently used. This involves injection of a scale inhibitor into the producing formation through the production tubing string under pressure. The scale inhibitor molecules adsorb to the formation, to be gradually released with the produced fluids. Scale inhibitor squeeze applications can last for periods up to six months. The need for renewed treatment is determined through tests for inhibitor residual in the produced fluids.

Mineral Scales in Steam Injection/Thermal Systems

Once through steam generators (OTSGs) for oil field use is designed to tolerate higher boiler feed water dissolved solids and the resulting deposit formation than conventional drum boilers. In addition to the challenges created by the feedwater chemistry, the high cycles of concentration (COC) at which these systems operate create very high levels of super saturation with a greater tendency to form deposits. OTSGs and HRSGs tend to operate at 3 to 5 COC (using poorer feedwater quality compared to a conventional boiler at comparable pressure) while evaporators can operate from about 6 to 50 COC.

Composition by XRF	Location Number			
	1	2	3	4
SiO_2	15	17	12	45
CaO	4	7	2	1
MgO	9	10	5	6
Na_2O	< 1	2	1	2
Fe_3O_4	15	5	2	14
P	3	5	0	0
S	4	5	1	2
Carbonate		< 1	< 1	< 1
Total Inorganic	54	49	24	72
Loss at 925°C	46	51	76	28
Total Organic (C,H,N)	42	42	67	26
Sample Source	Pigging	Tube	Pigging	Tube

[*] HRSG, heat recovery steam generator operating as once-through system.
[†] Lithium species are not directly detected by XRF.

Table 34.3 % Composition of Tube Deposits and Pigging Samples (OTSGs, HRSGs[*], by XRF[†])[2]

Composition and nature of deposits formed during operation of OTSGs can be identified from samples obtained from pigging operations or from tube samples received for metallographic analysis. Deposits obtained from heat-transfer tube surfaces and pigging samples are measured by X-ray fluorescence (XRF), X-ray diffraction (XRD), and C/H/N analysis. Those tests are used to determine percent levels of chemical ions (inorganic and organic) and any crystalline mineral species present in the deposit. Tables 34.3 and 34.4 summarize analyses from several tube and pigging deposits found in systems using high silica feedwater.

Hardness, Iron, and Silica Scales

By their very nature, thermal processes used to remove bitumen result in large volumes of silica-laden PW that must be treated for reuse [2-to-9 volumes of steam (cold water equivalent) are injected

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[2] Ralph, C.K., Hoots, J.E., Batton, C.B., Silicate Deposit Control in Steam-Assisted Gravity Drainage (SAGD) and Produced Water Applications, Nalco an Ecolab Company, IWC paper 12–40, 2012.

Mineral Species (observed by XRD)	Location Number			
	1	2	3	4
Lizardite [$Mg_3Si_2O_5(OH)_4$]	X	X		
Ferrorichterite [$Na_2CaFe_5Si_8O_{22}(OH)_2$]			X	
Sodium Magnesium Silicate Hydroxide [$Na(Na,Mg)Mg_5SiO_8O_{22}(OH)_2)$]			X	
Lithium Silicate (Li_2SiO_3)				X
Alpha-quartz (SiO_2)	X			
Magnetite (Fe_3O_4)	X	X		
Hematite (Fe_2O_3)		X		
Wustite (FeO)			X	
Iron Sulfides ($Fe_{(x)}S_{(y)}$)	X			
Hydroxylapatite [$Ca_5(PO_4)_3(OH)$]	X	X		

Table 34.4 Mineral Composition of Tube Deposits and Pigging Samples (OTSGs and HRSGs by XRD)[3]

per volume of bitumen recovered with a cumulative steam-to-oil ratio ranging from about 2:1 to 9:1][4]. The majority of the feedwater are a direct result of recycling the PW, however, supplemental water containing high hardness levels (calcium, magnesium) are needed to maintain the correct water balance. The mixing of waters containing hardness and silica in conjunction with equipment operating conditions can directly lead to silicate-based deposits forming inside plant equipment. Iron salts, also present in under-ground formations or from system corrosion, adds the potential for iron based silicate deposit formation during transferring and storing water.

Aluminum ions (Al^{+3}) and high salinity (Na^+) can be present, often leading to their incorporation into the silicate deposits. Also, low concentrations (mg/L) of nonhardness ions (e.g., lithium, Li^+) can form insoluble silicate-based deposits.

Several unit operations in thermal plants (boilers, OTSGs, HRSGs, evaporators, and waste-disposal) typically run at high COC, which dramatically increases the possibility that silicate-based deposits will form. Once silicate-based deposits form inside plant equipment,

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[3] Ralph, C.K., Hoots, J.E., Batton, C.B., Silicate Deposit Control in Steam-Assisted Gravity Drainage (SAGD) and Produced Water Applications, Nalco an Ecolab Company, IWC paper 12–40, 2012.

[4] Tristone Capital Inc., SAGD: Looking Beneath the Surface, Energy Investment Research, 2007.

those deposits are tenacious and prove to be very difficult to remove. Deposit formation often reduces heat-transfer efficiency/equipment output. In many cases, this may lead to tube failures and unexpected equipment shutdown. The result is a negative impact on steam generation and ultimately oil production.

Even when unit operations are generally running within specification, deposit forming conditions can still exist due to high levels of silica/hardness/iron occurring from upset conditions. This can occur over relatively long periods of time or may occur as numerous short episodes at random times.

Oil and Other Organic Components

One additional complication to the deposit formation in thermal systems is that the feedwater can contain organic constituents such as bitumen, oil, and organic carbon. Often the deposits formed are primarily inorganic with a significant percentage of organics present. This organic portion of the deposit is often generically referred to as coke.

We know from conventional drum boilers that when oil gets into a boiler, it will stick and cause all kinds of problems. Looking at free oil is a good way to monitor how the oil separation process is going and predict if oil-related coke formation may occur. Soluble organics appear to be involved too, although not all water-soluble organics will form coke. The chemical and mineral composition of coke deposits is exceedingly complex.

Scale Removal and Prevention

OTSGs and once-through HRSGs for oil field use are designed to tolerate higher levels of deposit formation, as they are relatively easy to clean by mechanical methods (pigging). Evaporators typically rely on chemical washes and mechanical cleaning once deposition becomes sufficient to impede system operation. Whether it's an OTSG, HRSG, or evaporator; mechanical cleanings can be expensive and time consuming. Downtime for the cleanings results in substantial lost production. In many instances, continuous treatment of the water stream with polymers or chelant treatments can prevent or reduce scale formation.

Corrosion

Water Injection Systems

The primary corrodents in oilfield water systems are carbon dioxide (CO_2), hydrogen sulfide (H_2S), and oxygen (O_2).

Oxygen is corrosive even at low concentrations because of its participation in creating differential cells beneath deposits on metal surfaces, which become anodic to adjacent deposit-free areas. Control of oxygen corrosion in oilfield water systems requires a conscientious effort to exclude air from all surface tanks and vessels and from the casings of producing wells. Field gas is used to maintain a positive gas blanket in these areas whenever possible.

After establishing control over oxygen exposure, it is then practical to use an oxygen scavenger to react with trace quantities of remaining oxygen. Several types of sulfite are commonly used, including sodium bisulfite ($NaHSO_3$), ammonium bisulfite (NH_4HSO_3), sodium sulfite (Na_2SO_3), and sulfur dioxide (SO_2).

The chemistry is the same with all forms; the sulfite reacts with oxygen to form sulfate:

$$SO_3^{-2} + \frac{1}{2}O_2 \rightarrow SO_4^{-2} \tag{34.4}$$

The sulfite–oxygen reaction is influenced by temperature and pH. Optimum pH for quick reaction is above 7. Most oilfield waters will range in pH from 6.0 to 7.5.

Catalysis of the reaction is necessary. Sometimes, naturally occurring metal ions in the PW act as effective catalysts, but usually the catalyst is provided in the sulfite formulation.

Whenever H_2S is present, iron sulfide will deposit. The resulting deposits are cathodic to base metal, so it usually follows that severe pitting occurs beneath iron sulfide deposits, all because of the H_2S. Where O_2 intrudes into a sulfide system, the rate of corrosion can become uncontrollable. Carbon dioxide mixed with H_2S is also much more aggressive than either of the gases alone. Where H_2S is present, an efficient film-forming inhibitor must be used to prevent severe, localized corrosion. Hydrogen sulfide is corrosive because it ionizes to form a weak acid:

$$H_2S \rightarrow H^+ + HS^- \tag{34.5}$$

Invariably, corrosion inhibitors used in oilfield applications are organic film formers. The molecules adsorb onto metal surfaces to shield the metal from corrodents. Since the film-forming corrosion inhibitors must be added to a wide range of brine concentrations and in many cases to a mixture of water and hydrocarbon, inhibitors with a wide range of solubility must be used. In the producing well, where a mixture of crude oil and brine must be treated, an inhibitor that is oil soluble and only slightly water dispersible is often required. This will film metal from the oil phase, providing long-term persistency to the metal surface, that is, the film will be maintained even when the inhibitor feed is discontinued. This allows batch treatment of producing wells in many instances. One of the most common methods of treating producing wells is using a treating truck to pump inhibitor down the tubing or into the annulus, followed by a flush of PW. The application is repeated periodically at intervals depending on the aggressiveness of the corrodents.

In injection water systems where water is the predominant phase, inhibitors must be either water soluble or highly water dispersible in order to carry through the surface line and tubing system. These inhibitors are not persistent, and it is necessary to feed continuously, always maintaining a residual in the system. Loss of inhibitor residuals results in desorption of inhibitor film and loss of protection.

In monitoring the chemical program, inhibitor residuals are determined through field extraction tests.

Corrosion monitoring is usually accomplished through a combination of metal weight-loss specimens, corrosion meters, pipe spools or nipples (which have the advantage of duplicating flow conditions), and iron counts. Residual iron concentrations are valid in systems without hydrogen sulfide, where H_2S is present, iron is deposited as iron sulfide.

Steam Injection/Thermal Systems

The most common corrodents in oil field thermal systems is oxygen (O_2). Less commonly, hydrogen sulfide (H_2S) may become a corrosion issue. Some metal surfaces may also experience erosion–corrosion.

Oxygen is a highly active element. Even in small amounts, it can cause serious corrosion in lines, heat exchangers, and steam-operated equipment. Corrosion increases with increasing oxygen content. The corrosion rate of oxygen dissolved in water is significant as temperature rises above approximately 120°F (49°C) and doubles for each 18°F (10°C) increase. In addition, portions of a system that are exposed to high flow rates or turbulent flow conditions are more susceptible to oxygen attack. Oxygen is also responsible for creating scaling agents through oxidation of ferrous iron and hydrogen sulfide. It is important to try to exclude oxygen from all vessels, casings, and surface supply lines. Sulfite based oxygen scavengers are typically used to chemically treat residual oxygen in OTSG feedwater, but low solids alternative scavengers are more commonly used in evaporated feedwater.

Recently published data suggests that an erosion–corrosion mechanism may be operating across steam generator passes. Iron pickup can be highly variable and is thought to be affected by layered, porous, coke-rich deposits that form near the point where boiling begins and are intermittently released at varying rates over time. When released, these solid deposits are accelerated by the fluid flow in the steam generator and provide the abrasive force needed for the erosion–corrosion mechanism. The presence of hard silicate minerals within the coke matrix of the deposits makes the particles far more abrasive than pure coke without inorganic mineral inclusions.[5]

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[5] Godfrey, M.R., Desch, P., LaRocque, L., Erosion-Corrosion in Oil Field Once Through Steam Generators, Nalco Champion an Ecolab Company, IWC paper 14–53, 2014.

Pigging is performed widely in OTSGs to mechanically remove the scale and fouling material that decreases heat transfer efficiency. A pig is a scraping device designed to closely fit inside a boiler tube. The pig abrasively removes deposit from the internal surface of the tube when it is forced through the length of the tube. The pigging process generally cleans the tubes down to bare steel. The bare metal is initially more susceptible to corrosion and an OTSG will generate more corrosion products over a steam generating pass shortly after a pigging operation. Over time a bare steel surface exposed to the high temperature and high pH conditions of steam generation will spontaneously form a surface film of magnetite, Fe_3O_4, which is more protective against further corrosion.

Bacteria Control

Control of bacteria is important in oilfield water operations because bacteria can cause plugging of the injection water formation and serious corrosion. Bacteria are seldom an issue in thermal systems.

The most troublesome of these organisms is the anaerobic sulfate-reducing bacterium, *Desulfovibrio desulfuricans*. Present in many oil-bearing formations, it is involved in the chemical changes which occur during the formation of petroleum. It reduces inorganic sulfate (SO_4^{-2}) to sulfide (S^{-2}), which leads to iron sulfide precipitates.

Clostridia, another anaerobic sulfate-reducing organism, are not as prevalent as *Desulfovibrio*. *Clostridia* are reported to be thermophilic, preferring a temperature range of 131 to 158°F (55–70°C).

Several species of aerobic bacteria are also important, most of which are found in surface waters used to supplement PW in a waterflood. Some of the more important organisms are *Pseudomonas*, *Flavobacterium*, *Aerobacter*, *Escherichia*, and *Bacillus*. These form slime masses, which can cause plugging or which shield the anaerobic *Desulfovibrio*.

Iron bacteria are occasionally found in some waterfloods, the two major species being *Sphaerotilus* and *Gallionella*. These oxidize the ferrous ion (Fe^{+2}) to ferric ion (Fe^{+3}). Iron bacteria are identifiable through a microscopic analysis following staining.

Beggiatoa oxidize sulfide to sulfate and usually grow in open PW systems, where a gathering line dumps into an open pit. They are often responsible for filter plugging.

Microbes are controlled by chemical application. The concentration of chemical and the contact time vary among systems. Normally, chemical is fed at a selected dosage for a period of 4 to 8 hours. Following application, samples are withdrawn from the system, and microbial population is determined. The frequency of biocide application is dictated by such control tests.

In many situations, physical system cleanup is necessary to gain proper microbial control. Low spots in lines or tanks with bottom accumulations of sediment or debris protect bacteria from chemical contact.

Raw Water, Utility, and Cooling Water Systems

Raw water, utility, and cooling systems used by in-situ producers and upgraders are similar to those found in refineries with continuous operation incorporating a number of interrelated process units. They are discussed in detail elsewhere in the handbook and will not be discussed here.

Automation and Control of System Chemistry

Automation and control of steam and water system chemistry are still relatively new in oilfield systems. A limited number of sensors tolerant of oilfield conditions and chemistry currently exist. Development of reliable and accurate instrumentation has been hampered by the oil and color present in the feedwater, which consists largely of recycled PW. Traditional sensors are often fouled by oil and typical contaminant concentrations are often out of range for commercially available monitors.

Current trends appear to focus more on data management and analytics for system modelling and prediction. Canada's Oil Sands Innovation Alliance (COSIA) and others have various projects in progress to supplement system operation predictive analytics.

Recycle and Reuse

Examples of recycle and reuse are plentiful and varied in oilfield steam and water systems. Common reasons include water scarcity at remote locations, legislative restriction on fresh water usage, and economics of operation.

Produced Water

PW is by far the largest byproduct of oil and gas exploration and production. It is estimated that 15 to 20 billion bbl/year of PW are generated from nearly 1 million wells in the United States. Globally the estimates are more than 65 billion bbl/year.[6] In these cases the producer is faced with basically two choices when dealing with PW:

1. Reuse or recycle
2. Discharge it to the environment (including down-hole discharge)

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[6] Veil, John A., Pruder, Markus G. Elcock, Deborah, Redwelk, Robert, A White Paper Describing Produced Water from the Production of Crude Oil, Natural Gas and Coal Bed Methane (2004).

PW can be a complicated mixture containing some or all of the following; dispersed oil, dissolved or soluble organics, residual treatment chemicals, produced solids (clays, sand, and dirt), scaling metals (Groups 1A, 2A, and 3B in the Periodic Table), other metals, pH effects, sulfates and naturally occurring radioactive materials (NORMs). To release water to the environment, National Pollutant Discharge Elimination System (NPDES) discharge permits must be met. For environmental discharge, irrigation or water for livestock, BOD, salinity, TDS, oil content, heavy metals, and all must meet the NPDES permit.

To reuse the water in drilling applications, certain specifications must be met to ensure that it does not corrupt the well or other areas of potential use. In certain areas like fracturing, the water content plays a critical role in the choice and performance of fracturing chemistries.

In hydraulic fracturing operations, huge volumes of water are needed for well completion. Due to the enormous volumes of water needed for well completion there is a large economic incentive to reuse as much PW as possible during the fracturing, instead of relying on all freshwater. When reusing PW for hydraulic fracturing two major concerns in water quality are the amount of bacteria and iron in the PW. Bacteria in the PW are of concern as introducing SRB to the well during hydraulic fracturing can lead to souring of the well, creating a safety risk and decreasing the worth of the oil. High iron levels in the PW can lead to precipitates downhole that plug the well. PW can be treated with a peracid based biocide to control both bacteria and iron levels in PW. Peracid biocides are broad spectrum oxidizing biocides that kill bacteria by oxidizing proteins in microbial cells. The oxidizing nature of peracid biocides also will oxidize soluble iron in the water, producing particulate iron that can separate from the PW before it is used to formulating fracturing fluid.

Steam injection is a method of extracting heavy oil. There are at least three types of steam stimulation, CSS, Steam flooding, and the SAGD. The first two are most common and practiced throughout the world. The latter is practiced in the oil sands of northern Alberta. CSS is a 3-phase process consisting of steaming, soaking, and production. Steam flooding effectively uses steam to chase the oil from a steam well to a production well. SAGD uses two horizontal wells, the upper steams, while the lower collects the emulsified oil. The latter two use steam continuously, while CSS uses steam intermittently. In all cases, the emulsified oil is returned to the surface for processing where the oil is separated from the PW. In a majority of cases, the PW is further treated and then used to produce steam. In SAGD, PW is first treated with chemistries to break the oil out of the water, and then further treated to remove any residual oil. In Canada, the major scaling component is silica, so it is common to see a warm lime softener using magnesium Oxide to reduce Si concentration. In some cases, evaporators are used in place of the lime softener and effluent can be used for an OTSG or conventional boiler.

Transportation and Storage

The Midstream sector is an industry unto itself, linking the producers in the oil fields to the processers at the refineries. The modes of transport used to move these products include pipeline, marine tankers and barges, and rail and truck. Pipeline is the most common method of transport requiring compression pump stations to provide the motive force to move the products over thousands of miles of varying terrain and conditions.

The characteristics of the various crudes moved through these distribution systems often requires some remediation especially with the increased production of the unconventional oils. High wax or asphaltine content crudes typically will have flow problems such as poor pumpability or cold flow issues related to the viscosity of the oil. The use of additives such as viscosity modifiers, flow improvers, pour point depressants, and wax dispersants is critical to ensure that the products can be moved and stored in an efficient manner. In addition, corrosion inhibitors, biocides, and H_2S scavengers are also used to maintain the integrity of the distribution system or safety during handling. Some of these additives can be problematic at the end user especially in the treatment of the resulting waste.

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CHAPTER 35

The Refining Industry

Refining

Petroleum refining is a continuous operation incorporating several interrelated process units, each designed to either produce or enhance a finished product. Since water is used in the refinery for heating, cooling, and processing, it represents an integral component of the refining process. A refinery may draw water from a variety of sources, and the treatment processes used to condition this water vary accordingly. Little or no treatment may be required for some well waters, while other water sources may require extensive treatment incorporating clarification, softening, and filtration. The types of water treatment problems here are much the same as in other industrial applications. In general, the basic water flow scheme is illustrated in Fig. 35.1.

After initial processing, the water is usually divided into several streams for use throughout the refinery. At most locations, this water can be used directly as cooling tower makeup, with little or no further pretreatment. However, an extensive treatment scheme is usually necessary to produce the high-quality water required for boiler feed. Figure 35.2 shows a typical water system designed for a large refinery utilizing a surface water source as plant makeup. Although each refinery is unique in their water usage, it is not unusual for 70% or more of the water brought into the refinery to be used for the cooling of processes and the generation of steam. Consequently, these two systems are the first to be scrutinized closely when water conservation is desired.

Refinery processes are net consumers of heat, to the extent that 10 to 15% of the heat equivalent of the incoming crude is used in the refinery operations. This is provided by refinery by-products, including off-gases, residual oil, and coke, and in many cases supplemented by natural gas. A typical process heat balance is shown in Fig. 35.3. This does not include heat recovered in waste-heat boilers.

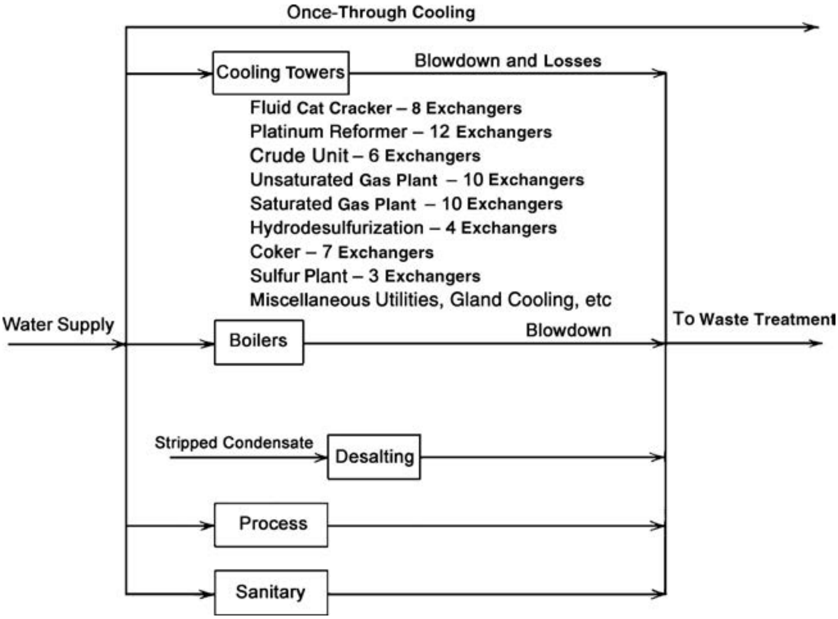

Figure 35.1 Water uses in a typical 150 000 bpd (23 800 m^3/d) refinery.

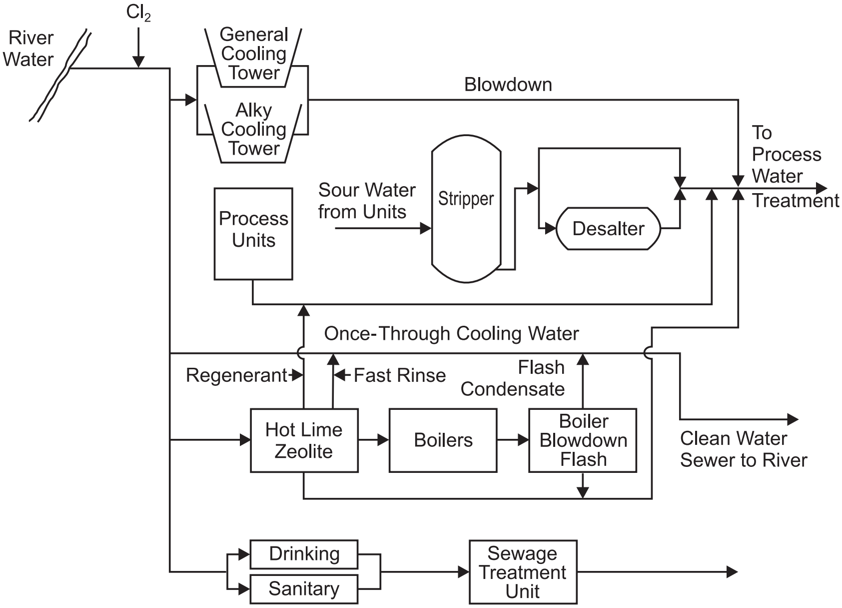

Figure 35.2 Water system treating surface water for refinery uses.

Source of Energy	Percent of Total Heat
Crude Oil	Nil
Distillate Oils	1.6
Residual Oil	9.0
LPG	1.3
Natural Gas	36.2
Refinery Gas	35.1
Coke	13.1
Steam (purchased)	1.1
Electricity (purchased)	2.6

Total heat required is approximately 674 000 Btu/bbl (4.47 GJ/m^3) of crude processed.

Source: From U.S. Bureau of Mines

Figure 35.3 Refinery heat balance.

Process Operations

The refining of petroleum products and petrochemicals involves two basic operations: physical change (separation processes) and chemical change (conversion processes). A refinery is a conglomerate of manufacturing plants, the number varying with the variety of products produced. The bulk of these products (kerosene, fuel oils, lubricating oils, and waxes) is fractions originally present in and subsequently separated from the crude petroleum. Some of these are purified and supplemented with nonpetroleum materials to enhance their usefulness. A refinery with half a dozen processes, including distillation and cracking, can produce gasoline, kerosene, and fuel oils. The manufacture of solvents requires two or three more processes; lubricating oil production requires at least five more; waxes require another two or more. Asphalts, greases, coke, gear oils, liquefied petroleum gases, alkylate, and all the other kinds of products that can be made would require as many as fifty different processes. Figure 35.4 is an overall flow diagram for a generalized refinery production scheme.

As previously mentioned refining is concerned with separation and conversion processes, carried out by individual unit operations. Basic to most of them are furnaces, heaters, heat exchangers, as well as distillation and extraction columns. Heat exchangers are typically of shell-and-tube design, often utilizing incoming hydrocarbon feedstock as a cooling medium for hot products. If additional cooling (trim cooling) is required, water is used.

Distillation and extraction are usually the principal techniques in product separation. Distillation separates various hydrocarbon mixtures into components having different boiling points. In extraction,

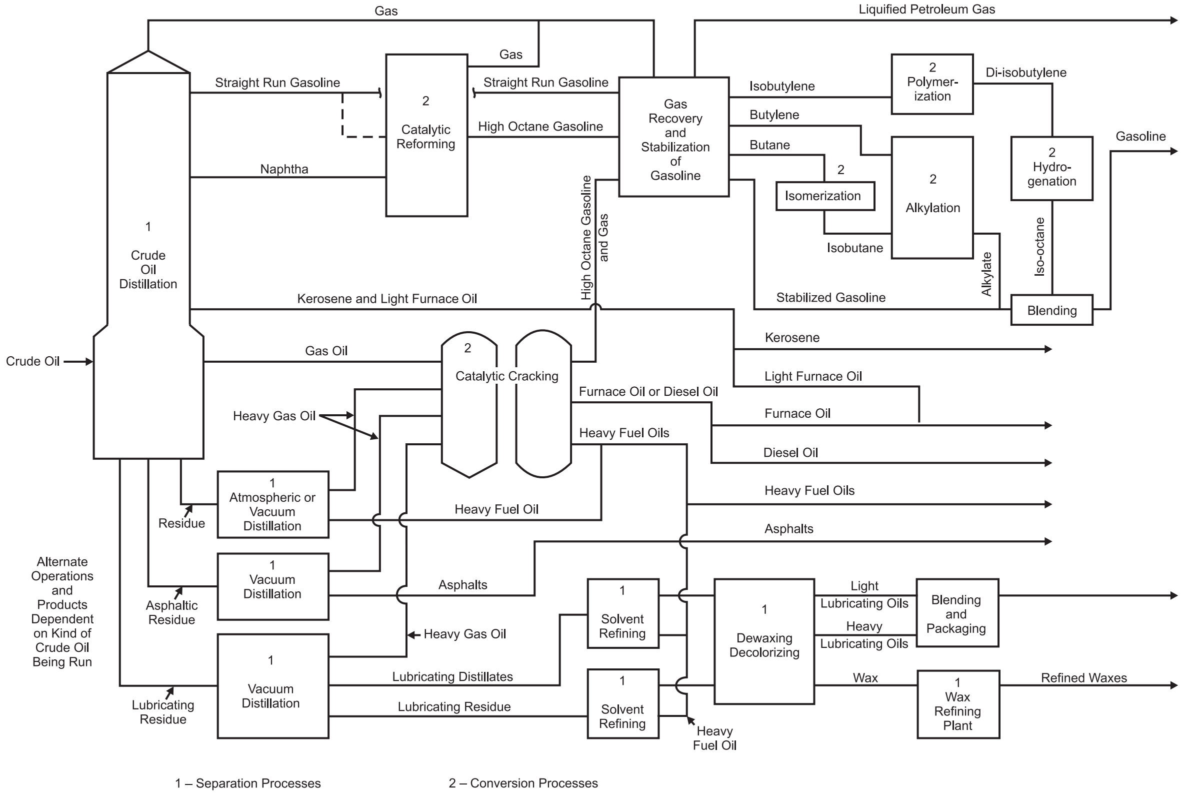

FIGURE 35.4 Generalized flowchart for petroleum refining. (*From Shreve, R. N., Chemical Process Industries, Third Edition, McGraw-Hill, New York, 1967.*)

hydrocarbons are separated based on their different solubility in a specific solvent. In some unit operations, filters are used to remove suspended contaminants from the hydrocarbon stream, such as catalyst fines and inorganic precipitates.

Distillation

Figure 35.5 illustrates a typical distillation column (pipe still). Preheated crude is charged into the bottom of a distillation column at a pressure slightly above atmospheric; the vapors rise through the column, contacting a down flow stream (reflux). As a result, the lightest materials concentrate at the top of the column, the heaviest materials at the bottom, and intermediate materials in between. Desired products are withdrawn at appropriate points. Because the lighter products (as vapor) must pass through the heavier products (as liquid) and must be in equilibrium with them at each point in the column, each stream contains some very volatile, low molecular weight components (light ends).

As indicated in Fig. 35.5, steam strippers are sometimes used to remove light ends from a sidestream. The sidestream is fed to the top

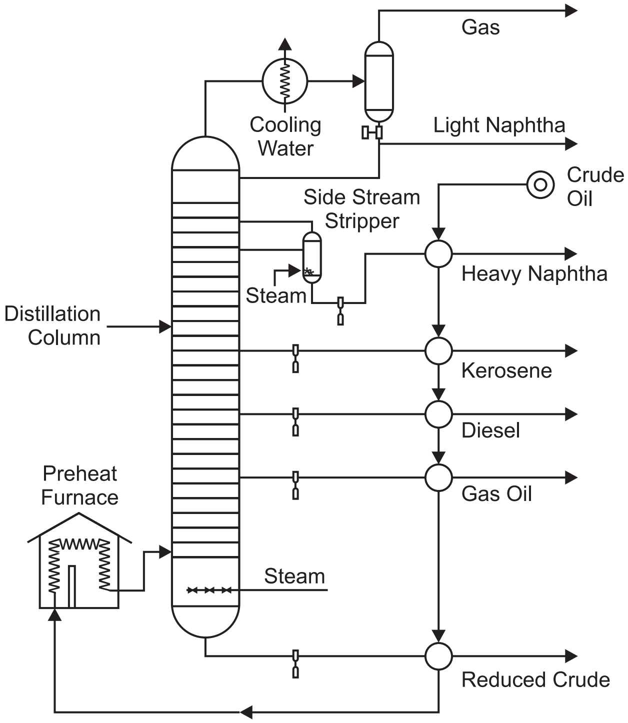

FIGURE 35.5 Distillation column with sidestream steam stripper.

of the stripper; counter-current steam strips out the light ends and carries them back to the main column.

The wastes from crude oil fractionation, and in general from most distillation columns, come from three sources. The first is the water drawn from the overhead accumulator before recirculation or transfer of the hydrocarbons to another fractionator. The water that separates from the hydrocarbons in these accumulators is usually drawn off and discharged to the wastewater treatment system. This water can be a major source of sulfides, especially when sour crudes are being processed; it may also contain significant amounts of oil, chlorides, mercaptans, and phenols. In addition to naturally occurring contaminates, there are many contaminates that are added during production of the crude oil, or added to reduce harmful existing crude oil contaminates such as hydrogen sulfide (H_2S). Some of these additives or additive byproducts are water soluble and can impact the wastewater treatment unit, such as amines and methanol. A second significant waste source is discharge from oil sampling lines; this oil should be separable, but may form emulsions in the sewer. A third waste source is the stable oil emulsion formed in barometric condensers used to produce a vacuum in some distillation units (Fig. 35.6).

Desalting

A refinery's desalting process is one of its most valuable assets. The desalter removes water-soluble contaminants and oil-insoluble

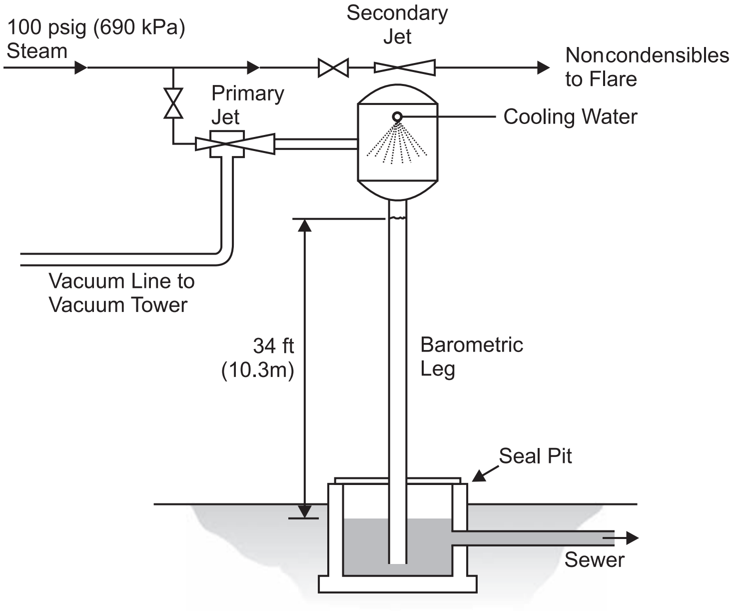

FIGURE 35.6 Barometric condenser.

FIGURE 35.7 Desalter unit.

particulates. It provides more protection to refinery equipment than any other single piece of process hardware (Fig. 35.7).

Contaminants found in crude come into the refinery from several sources. They may be inherent to the crude itself or to the producing field or they may have been introduced by the equipment and methods used to produce the oil in the field. They may have arisen as corrosion or erosion products when the oil was in transit from the field to the refinery. Contaminants also may be introduced in recovered oils and waste streams added to the crude for processing. Desalting is a two-step process, consisting of contacting and separation.

- Contacting mixes fresh water (4–10 vol%) with the crude so that the water contacts and dilutes all of the salts. Other solids also adhere to the water through a process called water wetting.
- Separation separates the diluted brine and solids from the oil as completely as possible, leaving the oil dehydrated, desalted and the water "de-oiled." The heavier water is then drained away to waste treatment. In many cases, the desalter brine effluent is processed through a sour water stripper before being discharged to waste treatment.

In vacuum towers, a steam jet ejector is the most widely used method for creating a vacuum. The steam and other vapors removed from the fractionator must be condensed, and the liquid removed before discharge of the vapor to the atmosphere.

The barometric condenser condenses the steam jet by use of a water spray in a closed chamber, and the water drains down the barometric leg. The organics, oils, and steam condensate are intimately

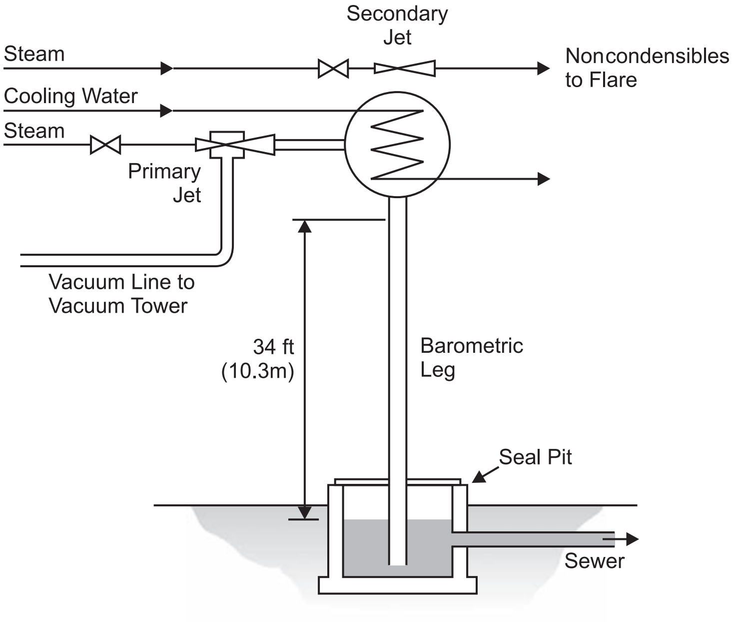

FIGURE 35.8 Tubular steam condenser.

mixed in a large volume of cooling water, which tends to form difficult to handle emulsions. Most refineries use surface condensers instead of barometric condensers. These units consist of a series of shell-and-tube exchangers in which the condensables are removed, and the water for cooling does not come into direct contact with the condensate (Fig. 35.8). The water discharge from the distillation operation is sent to the refinery waste plant, sometimes through a separate oil separation unit.

Thermal Cracking and Related Subprocesses

In thermal cracking units, heavy oil fractions are broken down into lighter fractions by application of heat, but without the use of a catalyst. Production of gasoline is low, but middle distillates and stable fuel oils are high. Visbreaking and coking, the two major types of thermal cracking, maximize the production of catalytic cracking feedstocks, indirectly increasing gasoline production.

Oil feed is heated in a furnace to cracking temperatures, and the cracked products are separated in a fractionator (Fig. 35.9). The heat breaks the bonds holding the larger molecules together, and under certain conditions, some of the resulting smaller molecules may recombine into larger molecules again. The products of this second reaction may then decompose into smaller molecules, depending on the time they are held at cracking temperatures.

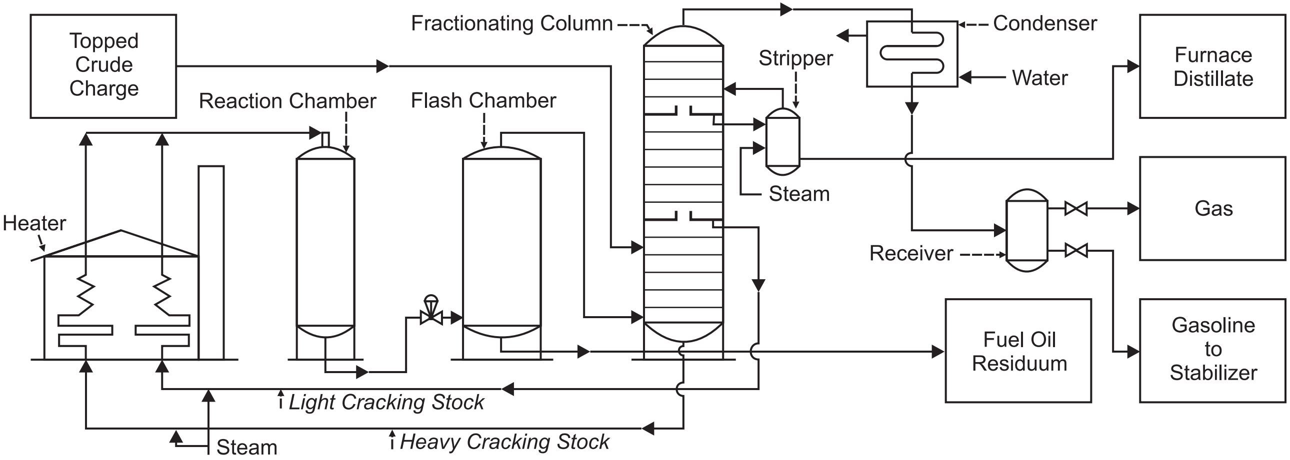

FIGURE 35.9 A thermal cracking process treating topped crude (Universal Oil Products process). *(From Shreve, R. N., Chemical Process Industries, Third Edition, McGraw-Hill, New York, 1967.)*

Visbreaking is a mild form of thermal cracking; it causes little reduction in boiling point, but significantly lowers viscosity. The feed is heated, cracked lightly in a furnace, quenched with light gas oil, and flashed in the bottom of a fractionator. Gas, gasoline, and furnace oil fractions are drawn off, and the heavier fractions are recycled.

Residual oils may be cracked to form coke as well as the usual gaseous and liquid products. The most widely used process, known as delayed coking (Fig. 35.10), accounts for about 75% of the total oil coking capacity.

Thermal cracking units require cooling water and steam on the fractionating towers used to separate products. Some towers employ steam stripping of a sidestream to remove light ends, requiring an overhead condenser and accumulator system for product/wastewater separation. Wastewater usually contains various oil fractions and may be high in pH, biochemical oxygen demand (BOD), chemical oxygen demand (COD), ammonia (NH_3), phenol, organic acids, and sulfides. Another important water use area is the high-pressure water sprays used for coke removal in delayed coking. Several refiners have instituted water recycle clarification systems to minimize water discharge from these coking units (Fig. 35.11).

Catalytic Cracking

The fluid catalytic cracking process is the most widely used refining process (Fig. 35.12). A large mass of finely powdered catalyst contacts the vaporized oil in the processing unit. The catalyst particles are of such a size that when aerated or "fluffed up" with air or hydrocarbon vapor, they behave like a fluid and can be moved through pipes and control valves.

In the catalytic cracking process (Fig. 35.13), feed and regenerated equilibrium catalyst flow together into the riser reactor. The cracked vapors from the reactor pass upward through a cyclone separator, which removes entrained catalyst. The product vapors then enter a fractionator, where the desired products are removed and heavier fractions recycled to the reactor. Spent catalyst passes from the separation vessel, downward through a stream stripper, and into the regenerator where carbon deposits are burned off. The regenerated catalyst again mixes with the incoming charge stream to repeat the cycle. On units using a carbon monoxide (CO) boiler, partial combustion in the regenerator is used. This incomplete combustion produces a preponderance of CO over carbon dioxide (CO_2). Significant amounts of hydrocarbons and other substances also remain unburned in the combustion gases. The CO and hydrocarbons in the exhaust make it a useful fuel. Most refineries burn this exhaust gas in specially designed CO boilers to generate steam. The gas burned in the CO boiler carries a significant amount of residual catalyst fines, which can cause furnace deposits.

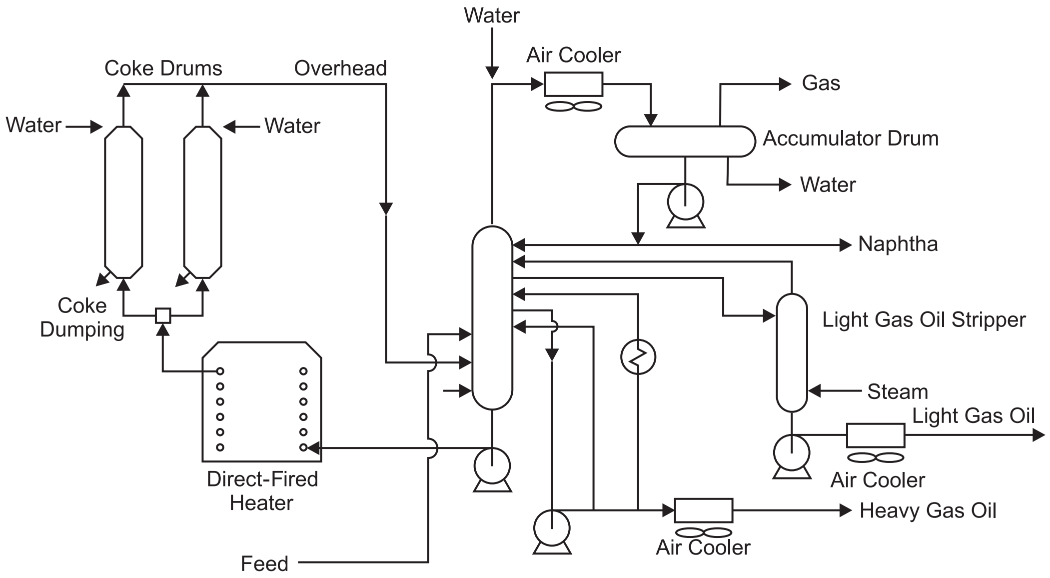

Figure 35.10 Delayed coking process.

FIGURE 35.11 Coker unit.

Today, most units operate in a complete combustion mode in the regenerator. This reduces carbon on regenerated catalyst, improves product yields, and helps reduce preheat fuel requirements.

Most fluid catalytic cracking units process vacuum and coker gas oils as feed. These feeds contain low levels of nickel (Ni) and vanadium (V), which are serious catalyst poisons. Heavy oil units, which use part heavy oil for feed, may operate with more than 2000 mg/L Ni and V on the equilibrium catalyst. This is made possible by using

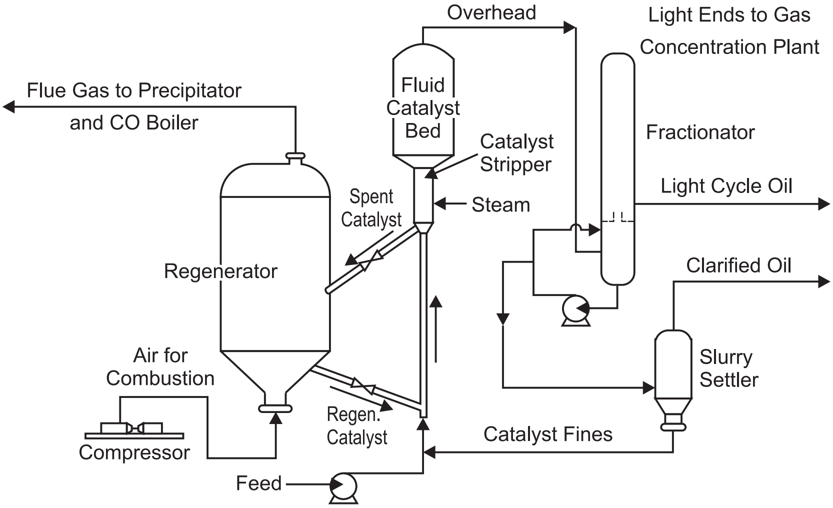

FIGURE 35.12 Fluid catalytic cracking unit.

Figure 35.13 Fluid catalytic cracking unit.

a metal passivator, which decreases the dehydrogenation poisoning activity of Ni and V.

The catalytic cracker is one of the largest producers of sour water in the refinery, coming from the steam strippers and overhead accumulators on the product fractionators. The major pollutants resulting from catalytic cracking operations are BOD, oil, sulfides, phenols, ammonia, and cyanide.

Catalytic Reforming

In catalytic reforming (Fig. 35.14), the object is to convert straight chain organics into cyclic molecules (aromatics of high octane). Reforming is essential to production of high-octane gasoline. Platforming, the most widely used reforming process, includes three sections:

1. In the reactor heater section, the charge plus recycle gas is heated and passed through reactors containing platinum catalyst.
2. The separator drum separates gas from liquid, the gas being compressed for recycling.
3. The stabilizer section corrects the separated liquid to the desired vapor pressure.

The predominant reforming reaction is dehydrogenation of naphthenes, or removal of hydrogen from the molecule. Important

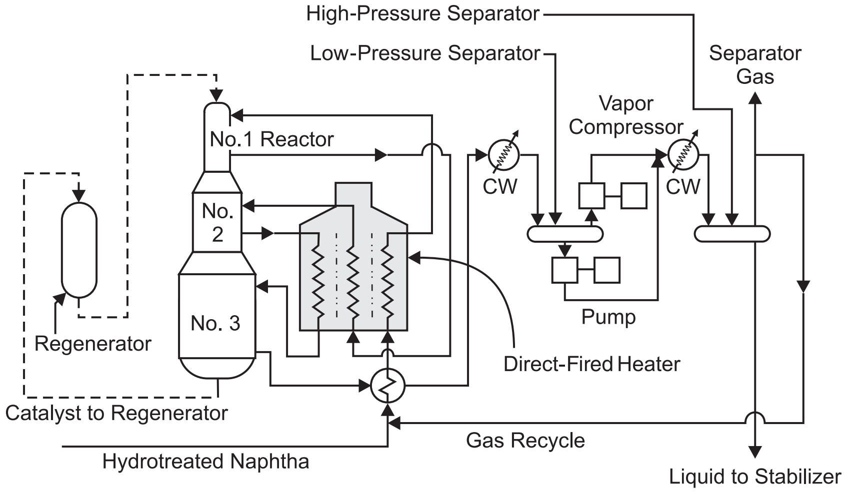

Figure 35.14 Catalytic reforming process.

secondary reactions involve rearrangement of paraffin molecules. All of these result in a product with higher octane ratings than the reactants. Platinum and molybdenum are the most widely used catalysts, with platinum predominating because it gives better octane yields.

Because platinum catalysts are poisoned by arsenic, sulfur, and nitrogen compounds, feedstocks usually are treated with hydrogen gas (hydrotreated) before being charged to the reforming unit. This produces hydrogen compounds, such as H_2S, which can be removed from the hydrocarbon stream.

Reforming is a relatively clean process. The volume of wastewater flow and the pollutant concentrations are small.

Alkylation

The amalgamation of small hydrocarbon molecules to produce larger molecules is known as alkylation (Fig. 35.15). In the refinery, this reaction is carried out between isobutane (an isoparafin) and propylene, pentylenes, and in particular, butylenes (olefins). The product is called alkylate. The olefin–isobutane feed is combined with the fractionator recycle. It is then charged to a reactor (contactor) containing an acid catalyst at a controlled temperature. The two predominant acid catalysts used are sulfuric acid and hydrofluoric acid. The contents of the contactor are circulated at high velocities to expose a large surface area between the reacting hydrocarbons and the acid catalyst. Acid is separated from the hydrocarbons in a recovery section downstream and recirculated to the reactor. The hydrocarbon stream is washed with caustic and water before going to the fractionating sections.

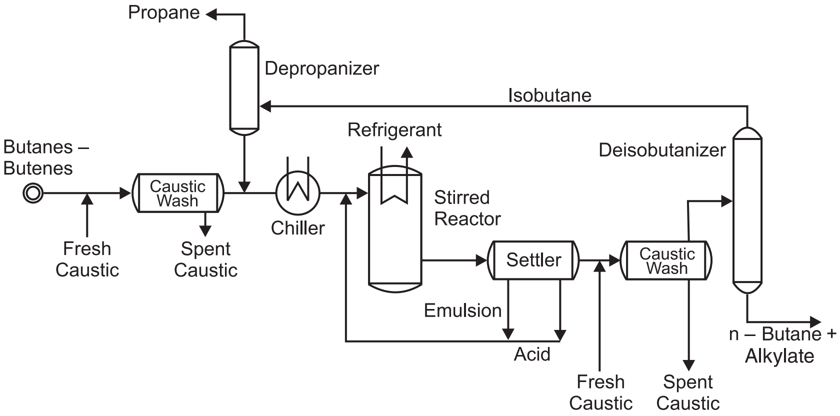

FIGURE 35.15 Alkylation process using sulfuric acid. (*Adapted from Hengstebeck, R. J., Petroleum Processing, McGraw-Hill, New York, 1959*.)

Isobutane is recirculated to the reactor feed, and alkylate is drawn from the bottom of the last fractionator (debutanizer).

Acid may contaminate the cooling water should heat exchangers leak. Water drawn from the overhead accumulators contains varying amounts of oil, sulfides, and other contaminants, but they are not a major source of waste in this sub process. The wastes from the reactor contain spent acids, which refineries may process to recover clean acids or may sell. Occasionally, some leakage to the sewer or cooling system does occur. The major contaminant entering the sewer from a sulfuric acid alkylation unit is spent caustic from neutralization of the hydrocarbon stream leaving the reactor.

Hydrofluoric acid alkylation units do not have spent acid or spent caustic waste streams. Any leaks or spills that involve loss of fluoride constitute a serious and difficult waste problem.

Sulfuric acid alkylation units usually have a chilled water refrigeration system with several compressors, which have critical shell-side cooling water on inter- and after-coolers.

Hydrotreating

Hydrotreating is mild hydrogenation (Fig. 35.16) that removes sulfur, nitrogen, oxygen, and halogens from a hydrocarbon feed and convert olefins (unsaturated hydrocarbons) to saturated hydrocarbons. Petroleum feedstocks ranging from light naphthas to lubricating oils are hydrogen treated. The major application of hydrotreating has been removing sulfur from feeds to catalytic reformers to prevent catalyst poisoning. Each of the different types of hydrotreaters, which vary in the selection of catalyst, incorporates a reactor and a separator. The oil feed, preheated to 400 to 700°F (204–371°C), passes through a

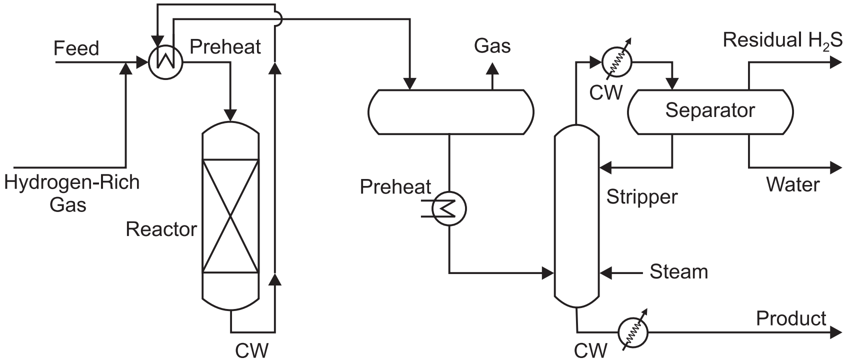

FIGURE 35.16 Hydrotreating process.

fixed-bed reactor, where it combines with hydrogen in the presence of a regenerable metal oxide catalyst at 200 to 500 psig (1.4–3.4 MPag). The product stream is cooled before entering a separator, where excess hydrogen gas is separated for use in other operations. After separation, the product is steam stripped for removal of residual hydrogen sulfide (Fig. 35.17).

Major wastewater streams come from overhead accumulators on fractionators and steam strippers and sour water stripper bottoms. The major pollutants are sulfides and ammonia. Phenols may also be present, if the boiling range of the hydrocarbon feed is high.

FIGURE 35.17 Vacuum residue hydrotreater reactors.

Utility Systems

The steam generating system is the heart of the refinery operation, since steam is a major source of energy in the refinery. It is used to drive pumps and compressors, to heat process streams, to strip sour water and can represent up to 35% of the water use in an average refinery. A typical steam system is shown in Fig. 35.18.

The pretreatment of boiler feedwater is one of the most important steps in efficient boiler operation. The specific pretreatment scheme for a steam generating system is dependent on such factors as boiler design, steam requirements, heat balance, outside power costs, and future expansion. Many refineries use hot process softeners, filters, ion exchange trains, and reverse osmosis units to prepare their boiler makeup. The selection of the appropriate pretreatment equipment will ensure that the steam generators can operate at optimum cycles of concentration with a low risk of failure. Incorrect matching of pretreatment with the boiler water requirements will result in lower cycles of concentration, higher water usage, and high operating costs.

Additional steam is generated in heat recovery and process heat boilers. These boilers can be found throughout the refinery in the various process units. Process heat boilers or kettles often resemble shell-and-tube heat exchangers in design but without the more sophisticated steam separation equipment found in conventional boilers. These small boilers can represent a significant volume of low pressure steam but can also be a major source of steam contamination. In most refineries, the steam generated by the process usually condenses as an acceptable quality condensate for return to either the boiler that produced it or to the general condensate return system. The major concern in these systems is prevention of corrosion in the condensate systems, particularly at the point of initial steam condensation. Depending on the pressure of the system, a condensate polishing unit may be installed to remove oil, corrosion products, or both, before returning this water to the boiler.

One source of condensate that is problematic is condensate being returned from a methane reformer or hydrogen plant. Excess steam used in this process is recovered as condensate and returned to the boiler feedwater system. Traditionally, the returned condensate is laden with carbon dioxide, typically resulting in a pH of approximately 4.3. In addition, this condensate is also rich in organics and organic acids. This process condensate is mechanically treated for CO_2 removal prior to use as boiler feedwater. Even after CO_2 stripping, the residual CO_2 content as well as the organic acid content of this condensate results in unacceptably low pH conditions for the typical carbon steel feedwater system. Untreated, this feedwater condition will result in unacceptable preboiler corrosion. Due to the organic acid content, the preferred pH adjustment treatment is the use of dilute caustic feed of high purity caustic with feedback on

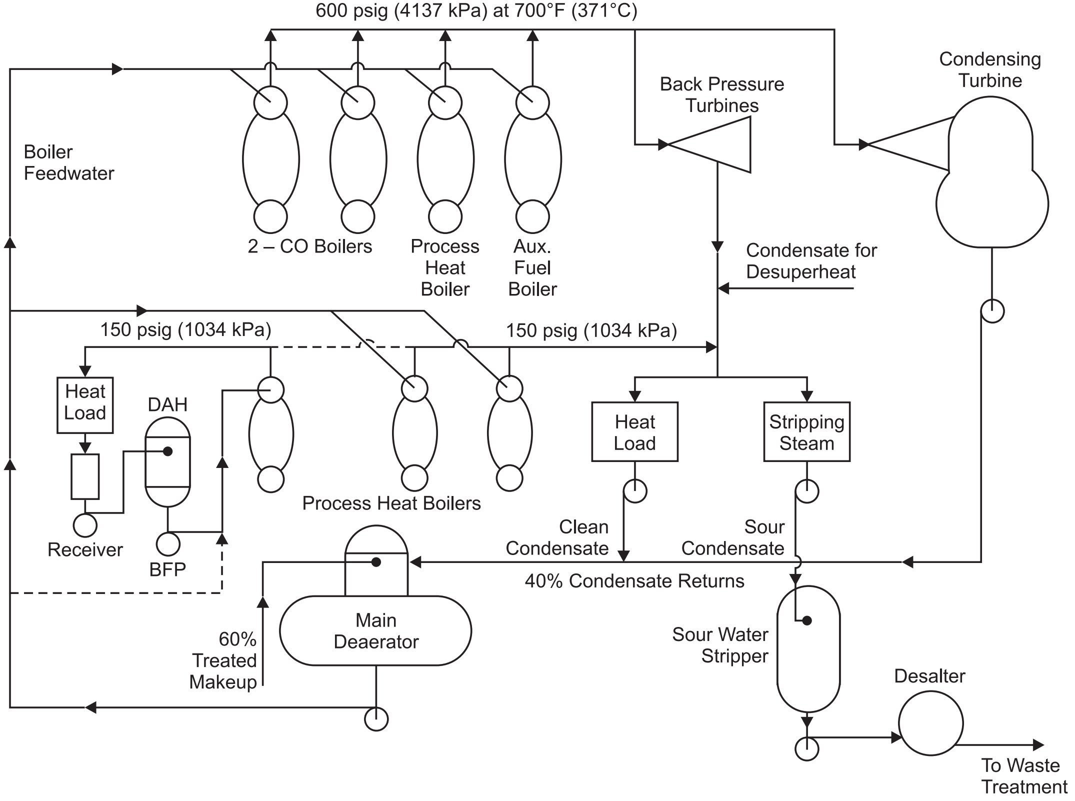

FIGURE 35.18 Process steam uses and condensate recovery in a typical refinery.

feedwater pH for monitoring/control. Amines can also be used but at the expense of more ammonia generation in the system.

Cooling Water Systems

The cooling requirements of a refinery demand a large volume of water. It has been estimated that 50 to 60% of the total water requirements in a refinery are for cooling. The cooling systems in a refinery are similar to those found in many manufacturing plants, involving once-through, open recirculating, and closed cooling circuits. While each of these systems can be found in the refinery, the open recirculating system serves the greatest demand for process cooling. Once-through cooling, while not common can be found in refineries adjacent to large bodies of water, be it fresh, brackish or seawater.

Waste Treatment Systems

Refinery wastewater treatment systems separate pollutants from the water by physical, chemical, and biological means. Primary treatment consists of physical, and often chemical, processes where the gross waste load of oil and suspended solids are separated from the water. Secondary treatment removes much of the remaining organic and dissolved solid pollutants by biological treatment, which consumes and oxidizes organic matter.

There are a few physical, chemical, or biological methods known as tertiary treatment, including activated carbon adsorption and filtration. As pollution control regulations become more stringent, tertiary treatment methods will become more common.

Broadly speaking, a refinery wastewater system consists of:

- A drainage and collection system
- Gravity oil–water separators and auxiliaries to remove oil and sediment
- Treatment units or disposal facilities to handle segregated chemical solutions and other process wastes, and to control the effects of pollutants that have toxic properties

Figure 35.19 is a generalized list of wastewater sources; it also shows how they are segregated into various sewer systems to optimize reuse, and reduce overall treatment volumes to a minimum.

The oil-free sewer collects wastewaters that have not contacted oil and that are not subject to any other contamination for which treatment must be provided. Since these waters seldom contain significant oil contamination, they may bypass primary treatment and some may discharge directly into the refinery outfall. However, if collected in a common sewer, this flow may be mixed with oily waste after primary treatment to reduce the hydraulic load on the primary treatment system.

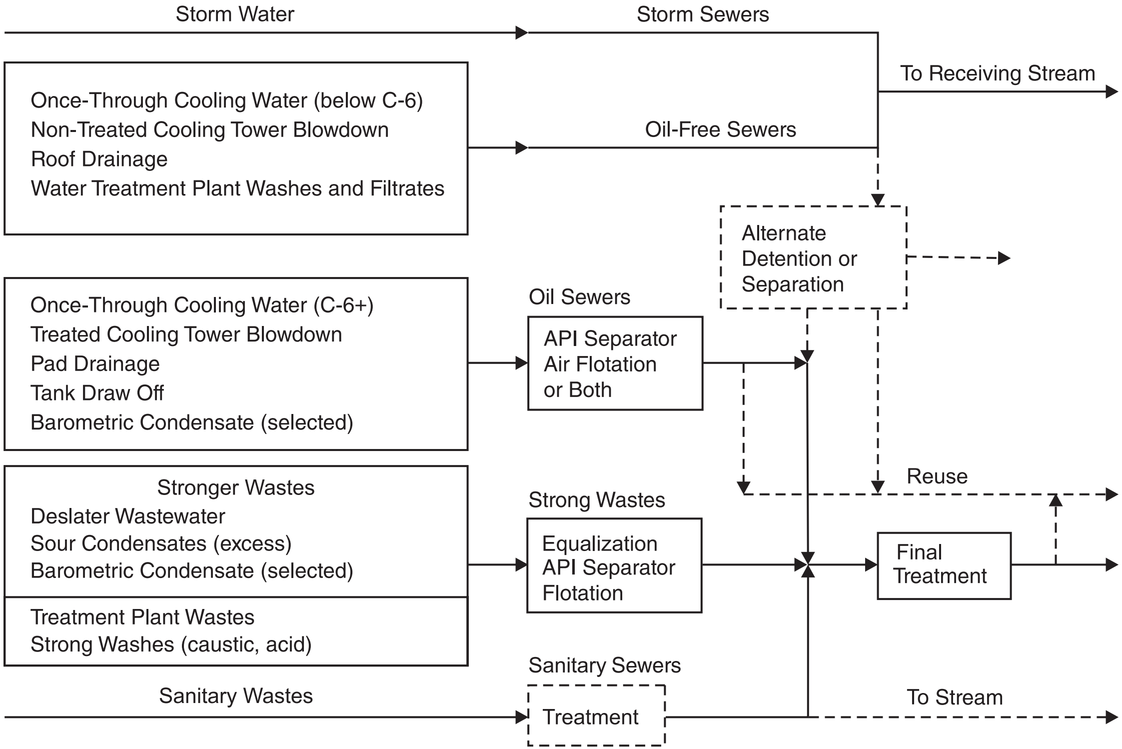

Figure 35.19 Suggested scheme for collection and treatment of refinery wastewaters.

The oily cooling water sewer system is intended to handle waters that are expected to be subject to minor oil contamination from leaks in heat exchange equipment or from spills. In the absence of contamination by chemicals or fine solids, which tend to cause emulsions, separation of any oil from the water can be readily accomplished. Barometric condenser cooling waters that are subject to contamination by easily separable oil, but not containing emulsified oil, may also be included in this system.

The process water sewer system collects most wastewaters that come into direct contact with oil, or that are subject to emulsified oil contamination, or chemicals limited by the plant discharge permit. Water from the process water sewer system can be treated in a variety of ways. It is not uncommon for the waste to pass through an API separator where solids are settled by gravity and insoluble oil is floated and removed. A polishing step, utilizing a floatation process such as induced air floatation (IAF) or dissolved air or gas floatation (DAF/DGF) often follows to ensure up to 90% removal of insoluble material. Pollutants remaining after gravity and floatation separation are reduced by secondary treatment methods.

Separator skimmings, which are generally referred to as slop oil, require treatment before they can be reused because they contain an excess of solids and water. Solids and water contents in excess of 1% generally interfere with processing.

The sanitary sewer system collects only raw sanitary sewage and conveys it to municipal sewers or to a separate refinery treatment facilities. State or local regulations usually determine the sanitary disposal requirements. Raw sewage can be used for seeding refinery biological treatment units.

Special systems include those required for the separate collection and handling of certain wastes, having physical or chemical properties that cause undesirable effects in the refinery drainage system, oil-water separators, or secondary treatment facilities. Spent solutions of acids and caustic, foul (sour) condensates, and degraded solvents are examples of such wastes.

Sour Water Stripping

Many wastewater effluents from petroleum refining processes originate from the use of steam within the processes. The subsequent condensation of the steam usually occurs simultaneously with the condensation of hydrocarbon liquids, and in the presence of a hydrocarbon vapor phase that often contains, H_2S, NH_3, hydrogen cyanide (HCN), phenols, and mercaptans. After separation from the hydrocarbon liquid, the condensed steam contains oil and a mixture of these contaminants. These wastewaters are typically called sour waters or foul waters, because of the unpleasant odor characteristic of dissolved hydrogen sulfide.

The amounts of these contaminants in a sour water stream depend on the type of refining process from which the stream originated, as well as the feedstock to that process and the pressure at which the steam was condensed within the process. The contaminant concentrations in typical sour waters will usually be 50 to 10 000 mg/L H_2S, 50 to 7000 mg/L NH_3, and 10 to 700 mg/L phenolics.

The principal contaminants in sour waters are hydrogen sulfide and ammonia, ionized as HS^- and NH_4^+, respectively. These can be removed by single-step steam stripping, which is a simple form of distillation for the removal of dissolved gases or other volatile compounds from liquids. Stripping is rather inefficient and requires large volumes of steam, because these ionized substances exert very little gas pressure unless the pH is adjusted. Stripping also removes phenolics to some extent, but the amount of phenolics removed may vary from 0 to 65%.

Effluent water from a sour water stripper is often reused as wash water makeup to the desalter.

Spent Caustic Treatment

Alkaline solutions are used to wash refinery gases and light products; the spent solutions, generally classified as sulfidic or phenolic, contain varying quantities of sulfides, sulfates, phenolates, naphthenates, sulfonates, mercaptides, and other organic and inorganic compounds. These compounds are often removed before the spent caustic solutions are added to the refinery effluent. Spent caustics usually originate from batch operations, and the batches may be combined and equalized before being treated or discharged to the general refinery wastewaters. Precautions must be taken when disposing of any high pH material into a waste stream as the pH balance can change dramatically resulting in the potential for scale formation in the lines and equipment downstream of the injection point. Chemical treatment and/or neutralization will often be needed to prevent this from occurring.

Spent caustic solutions can be treated by neutralization with spent acid or flue gas, although some phenolic caustics are sold untreated for their recoverable phenol value. Neutralization with spent acid is carried to a pH of 5 to ensure maximum liberation of hydrogen sulfide and acid oils.

In the treatment of spent caustic solutions by flue gas, hydroxides are converted to carbonates. Sulfides, mercaptides, phenolates, and other basic salts are converted to hydrogen sulfide, phenols, and mercaptans at the low pH conditions caused by the flue gas stripping. Phenols can be removed and used as a fuel or can be sold. Hydrogen sulfide and mercaptans are usually stripped and burned in a heater. Some sulfur is recovered from stripper gases. The treated solution will contain mixtures of carbonates, sulfates, sulfides, thiosulfates, and some phenolic compounds. Reaction time of 16 to 24 hours is required for the neutralization of caustic solutions with flue gas.

CHAPTER 36

The Chemical Industry

The chemical industry manufactures more than 50 000 different products, making it the largest and most varied of all industries. The massive scope of chemical products ranges from alkali to xylene, and touches markets from fibers to pharmaceuticals. Most are used as basic materials in other industries, and some are used directly by consumers. This industry includes such diverse products as industrial gases, chlorine, resins, fibers, film, synthetic rubber, pharmaceutical ingredients, soaps, detergents, paints, coatings, and agricultural chemicals like fertilizers, herbicides, and pesticides.

Figure 36.1 shows the extensive interrelationships of chemical products using petrochemical processing as an example. Basic building blocks like monomers, ammonia, and hydrogen are derived from feedstock such as natural gas and petroleum. These basic building blocks are strictly sold on the basis of their chemical composition. The commodity chemical product of one supplier is readily interchangeable with that of any other. Organic intermediates represent the next step via further chemical conversion of the bulk petrochemicals. Sometimes, multiple steps are required to produce an intermediate of the desired chemical composition. All of these products in turn are used in downstream "fine chemical" derivatives. Fine chemicals are sold on the basis of their performance rather than their composition. They are produced batch-wise and not in a continuous process. Depending on the end use application, chemical compositions can vary between subgroups, and they are not considered interchangeable. Table 36.1 lists the major high-production chemicals produced in the United States under the classification of inorganic and organic compounds.

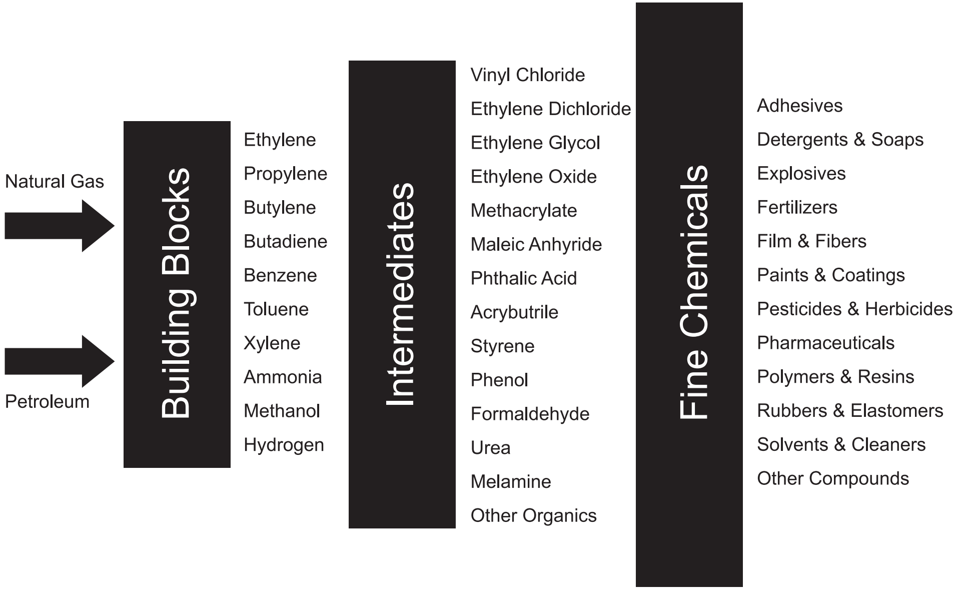

FIGURE 36.1 Chemical industry overview.

Organic		Inorganic	
Chemical	**Output**	**Chemical**	**Output**
Ethylene	24.0	Sulfuric acid	36.5
Propylene	15.3	Phosphoric acid	11.6
Urea	5.8	Chlorine	10.2
Ethylbenzene	5.3	Ammonia	9.8
Styrene	5.0	Sodium hydroxide	8.4
Ethylene oxide	3.2	Ammonium nitrate	6.4
Vinyl acetate	1.3	Nitric acid	6.3
Acrylonitrile	1.3	Hydrochloric acid	4.4

Source: Abstracted from Chemical Engineering News, July 10, 2006.

TABLE 36.1 2005 U.S. Production of Chemicals (Millions of Metric Tons)

Process Cooling Is a Major Water User

The chemical industry has the potential to use more than 324 million acre · ft (400 km^3) of water each year, with the vast majority used for cooling purposes. Water use varies widely within the industry. At the higher end, the manufacture of silicon nitride requires more than 15 000 lb (kg) of water to produce 1 lb (kg) of product. Several other products require in excess of 1000 lb (kg) of water to produce 1 lb (kg) of product. A number of the major commodity chemical products, including ammonia and ethylene, require 100 to 200 lb (kg) of water to produce 1 lb (kg) of product.

Table 34.2 shows the water usage by unit operation for several industry segments. The greatest use of water is for cooling process equipment. Many reactions generate heat, and the reaction vessel is cooled so that the temperature is controlled at the desired limit for production efficiency and product quality. Other chemical reactions require heat, and most chemical plants provide this with steam. If the steam is used only for low-temperature process heat, the plant may operate a low-pressure boiler; but if the plant requires a great deal of electric energy as well as heat, it is common to install high-pressure boilers to generate power through steam turbines, with the turbines exhausting into a process steam line, with perhaps some of the steam going directly to a turbine condenser. Chemical production is the second largest consumer of water treatment chemicals in North America. Many chemical plants are converting to cogeneration using high-pressure process steam to generate electricity for resale to the power grid.

Segment	Water Used [lb/lb (kg/kg) of Product]				
	Cooling Water	Process Water	Steam	Total Water Use	Typical Consumptive Use
Ethylene	198	3.6	14.5	216.1	10–30
Phosphoric acid	135	4.2	1.3	140.5	10–20
Propylene	135	2.4	0.8	138.2	9–18
Polyethylene	82	0.5	0.4	82.9	4–9
Chlorine	70	3.0	1.8	74.8	6–12
Sulfuric acid	66	0.4	0.4	66.0	3–7

Source: 2002 Process Economics Program (PEP) Yearbook International, published by SRI Consulting.

Table 36.2 Water Usage by Chemical Industry Segment

Cooling water is usually reclaimed by the use of cooling towers, so the requirement for makeup water is minimized. Most heat exchangers use water on the tube side. However, in some chemical processes, it is more suitable to have water on the shell side, with process fluid on the tube side. In this latter design, the cooling water is more likely to create deposit problems, due to the lower velocity.

Another large use of water is for process applications, which may include hydraulic conveying, classification, washing, and equipment cleaning. Some water may become part of the finished product. Finally, provision is made in most chemical plants for fire protection. This usually requires water applied either directly as a fog, or as a component in foam.

Chemical plant operations are classified into unit operations (such as evaporation, drying, and crystallization) and unit processes (such as monomer production, sulfuric acid production, or catalytic cracking—all involving a number of unit operations). Because each chemical manufacturing plant differs so much from its neighbors, it is simpler to assess water and steam requirements for different classifications of chemical manufacturing plants.

In most chemical operations, there are a number of processing steps involved, in preparing raw materials for the reaction that produces the finished product. The raw materials may be crushed and then conveyed by water to classification devices such as screens, which may be operated either wet or dry. Soluble raw materials may be dissolved in water, or if gases, absorbed in water to facilitate the chemical reaction. The quality of water may be important; for example, the water may contain iron, which could catalyze a reaction, discolor the finished product, or precipitate to produce a turbid product.

After preparation, the ingredients may be charged to a reactor. This may be done batch-wise or continuously, depending on the volume of throughput, the value of the products being handled, and the economics of the alternative designs. If the reaction is endothermic, the reactor is usually heated with steam. If the reaction is exothermic, the reactor is designed so that the mixture is heated to a certain temperature before the reaction initiates. Thereafter, cooling is required to maintain the desired reaction temperature. Figure 36.2 illustrates a reaction vessel designed for both heating and cooling. The polymerization of organic materials is an example of a reaction requiring initial heating, followed by cooling to maintain a specified temperature. The chemical reaction does not always take place in a sophisticated reactor; it often occurs in a simple sedimentation vessel, similar to that used for lime softening of water.

Once the chemical reaction has taken place, additional processing is usually required to remove the unreacted raw materials or unwanted products. When these impurities are solids, typical solids/liquids separation processes are used. Depending on the nature of the solids to be removed, the choice may be sedimentation, filtration, or centrifugation. The solids removed are often washed for recovery of valuable residues (Fig. 36.3).

Reactors can be mild steel, stainless steel, or glass lined. Mild steel is used for noncorrosive and low purity products, such as

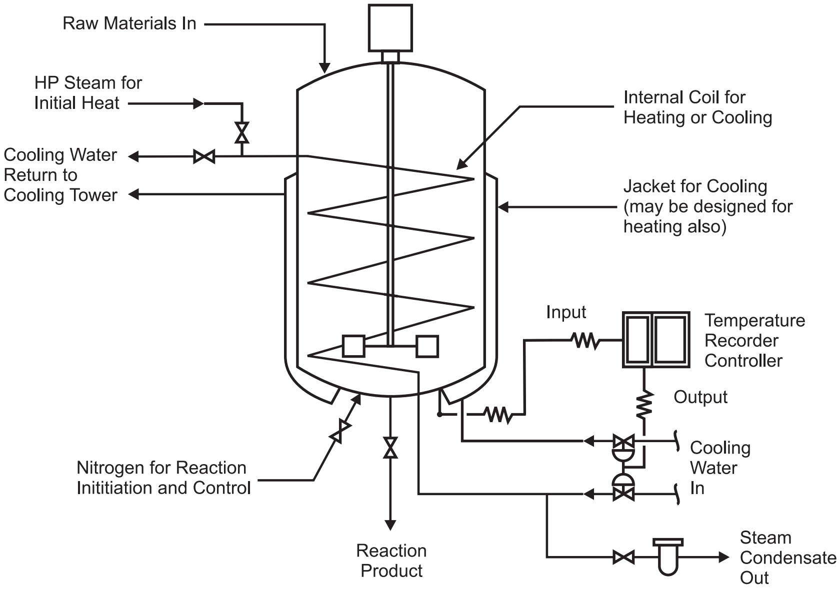

FIGURE 36.2 A reaction vessel designed for both heating and cooling of process materials.

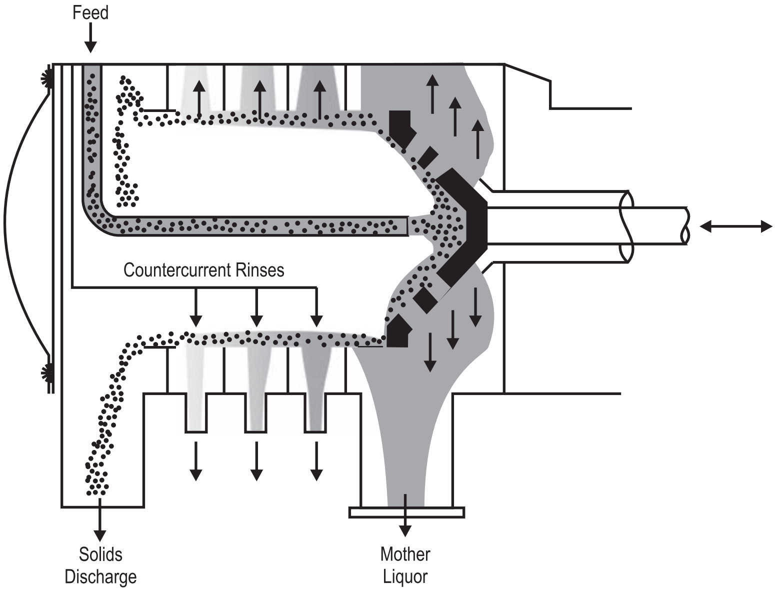

FIGURE 36.3 A pusher-type centrifuge designed for counter-current rinsing of solids for liquor recovery. (*Courtesy of Sharples-Stokes Division, Pennwalt Corporation*.)

polyvinyl chloride (PVC). Stainless steel jacketed reactors are used in many fermentation systems. Typically stainless steel vessels are used in biopharmaceutical manufacturing.

Glass-lined reactors are used when reactants are very corrosive or high-purity products are critical, such as pharmaceuticals. Jackets may be full or segmented plates, half pipe coils, or spirals wrapped around the outside of the vessel. Jackets may have nozzles that allow to increase fluid velocity and reduce fouling while improving the temperature profile and performance. Figure 36.4 shows fluids that may be present in a jacketed vessel. Figure 36.5 shows a typical full plate jacked reactor.

Many of the manufacturing processes using glass-lined jacketed vessels require heat to initiate the reaction. Once the reaction starts, it is exothermic, meaning the reaction generates excess heat, which must be removed to obtain the desired product quality and yield. The most aggressive corrosion and scaling conditions occur within the jackets when steam and cooling waters mix. Steam creates very high temperature, which leads to scaling when cooling water is added. The high temperature also increases the corrosion potential. Mixing steam and cooling water dilutes the corrosion and scale inhibitors in the cooling water, increasing the potential for corrosion and scale within the jacket. Water losses from the cooling tower and chilled

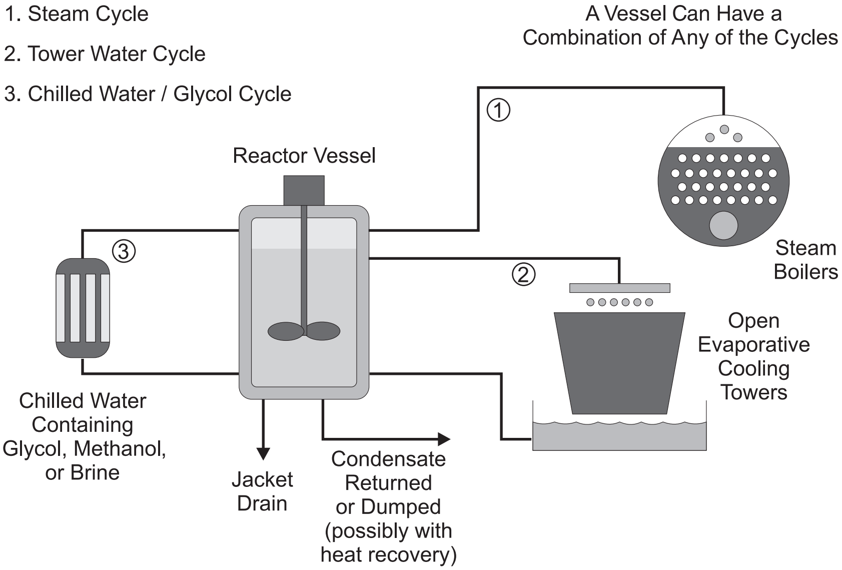

Figure 36.4 Possible series of fluids in a jacketed vessel.

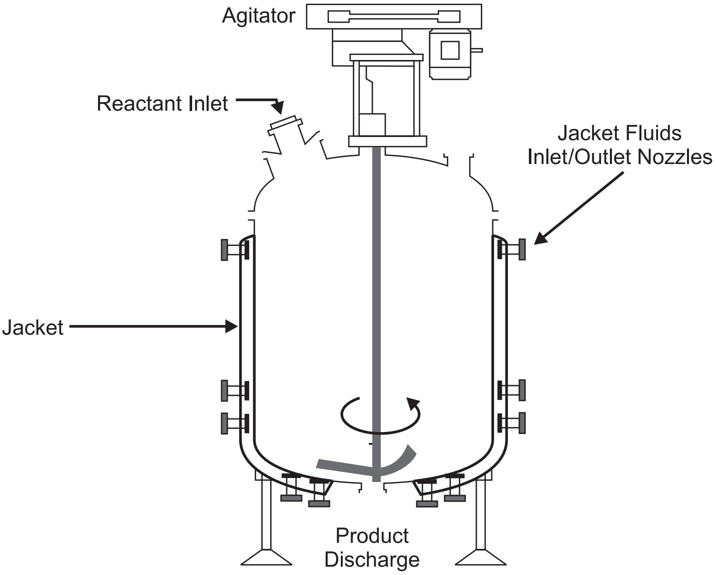

Figure 36.5 This is a typical jacketed reactor showing the reactant inlets, agitator, jacket product discharge, and jacket inlet and outlet nozzles for the heating and cooling fluids.

water systems complicate effective treatment. The treatment programs for the two cooling water systems must be compatible.

Typically, the steam cycle is first to heat the reactants and start the chemical reaction. The steam condensate might be recovered for boiler feedwater or discharged if not suitable to return to the boiler. If recovered, the steam condensate may be contaminated with cooling water containing hardness, which would cause scale in the boilers.

Cooling water might be used subsequent to the steam cycle in order to remove some of the heat of reaction and provide the desired temperature for optimum product quality and yield. Significant corrosion and scaling can occur as cooling water is added to the hot jacket containing steam condensate.

Chilled water or brine (glycol, alcohol, or salt) might be used as the next step if the reaction generates too much heat for the cooling water to maintain the desired reaction temperature. This step can result in mixing cooling water with chilled water or brine, having the undesirable effect of contaminating both systems. Figure 36.6 shows a typical jacketed reactor with both chilled water (CWR) and cooling tower (TWR) waters present.

Ideally, for good corrosion, scale, and biological control, the two waters should not mix, but this schematic shows that the two waters can mix.

Rather than mixing fluids within the jacket, some systems maintain a single fluid within the jacket, typically a synthetic heat transfer

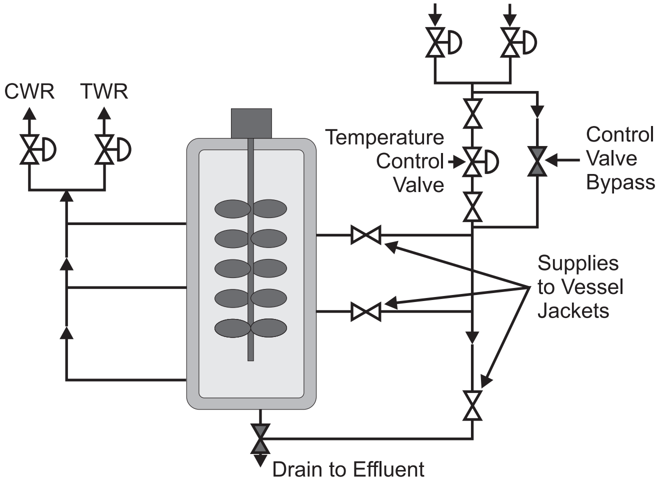

Figure 36.6 This schematic shows a typical glass-lined jacketed vessel with two different fluids used in the jacket—cooling tower water (TWR) and chilled water (CWR).

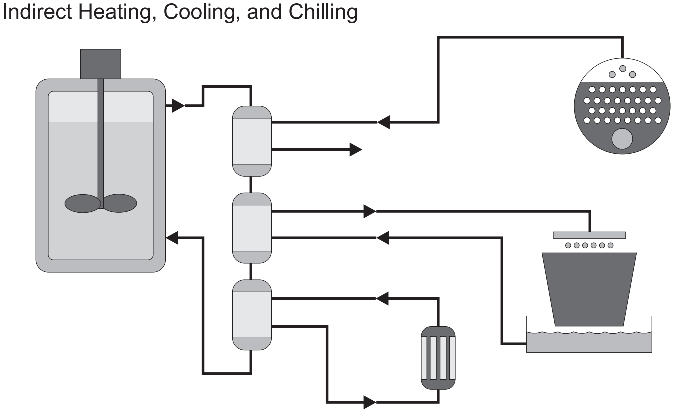

Figure 36.7 Indirect heating/cooling.

fluid like, Dowtherm, Syltherm, Therminol, closed loop water, or the like, and use heat exchangers to control the fluid temperature (Fig. 36.7). This arrangement prevents fluid mixing and subsequent severe corrosion and scaling issues in the jacket. Depending on the heat transfer fluid used, treatment, monitoring, and control might still be needed. The major disadvantage of this approach is the high capital cost for the extra heat exchangers and possibly additional pumps. Designing and installing these types of systems initially are gaining favor in new systems, but very few retrofits to an existing system are undertaken.

Contamination of the steam condensate with cooling water can force the disposal of valuable condensate or risk scale and corrosion problems in the boilers. Installing a heat exchanger can allow recovery of most of the heat from the steam condensate, but the water value, including the effect on the boiler cycles of concentration, is still lost.

Steam condensate, chilled water, and brine entering the cooling water periodically from batch reactor operations creates a difficult situation for maintaining good corrosion and scale control in the cooling water system. Any single condition can be handled, but variable conditions require automated feed and control systems to keep up with the constant changes.

Organic contamination, such as amines from steam and glycol or alcohol from brines, creates increased biological activity in the cooling water system, requiring an aggressive approach to biological control programs and adaptable feed systems.

Even with nozzles, as seen in Fig. 36.5, fluid flow within jackets is inherently low, increasing the potential for fouling and poor corrosion control.

Care must be taken when treating fluids, such as steam and cooling water, going to jackets. If treatment programs are not chosen and controlled correctly for all of the streams entering a jacket, a number of problems can develop, such as:

- Incompatible treatment products can react, deactivating both products. For example, neutralizing amines in the steam can react with halogen-based biocides in the cooling water.
- Direct injection of steam into cooling water dilutes the corrosion and scale inhibitors in the cooling water, reducing the treatment protection.
- Heating cooling water with steam, either directly by injection or indirectly with heat exchangers, raises the cooling water temperature beyond normal conditions, increasing the corrosion and scale potentials.

To provide good overall control, monitoring must be conducted on the outlet streams from the reactor jackets, not the bulk water systems. The goals in jacket water treatment should include:

- Start with clean reactor jackets. Clean metal surfaces are easier to control than dirty ones.
- Pretreating the clean jackets to minimize flash rust.
- Evaluating all fluid streams entering the jacket, including dilution effects and chemical interactions.
- Additionally, one water treatment supplier should treat all fluid streams entering the jackets so that all mechanical, operational, and chemical effects can be adequately evaluated and addressed.

If the impurities are not solids, then the final separation may require solvent extraction. This extraction may be accomplished with water if the process fluid is a hydrocarbon. Alternatively, the separation may be achieved by an operation involving a phase change such as evaporation, distillation, crystallization, or drying. In all of these operations, energy is applied to produce the separation, and cooling water may be used on the condensers or reflux heat exchangers (Fig. 36.8).

Process Flow Sheets

Many of the heavy chemicals listed in Tables 36.1 and 36.2 are used in water treatment processes. They are used in various pretreatment processes (softening, dealkalization, coagulation, disinfection, etc.), and their costs are minimal. Their use in pretreatment allows specialty water conditioning chemicals needed for cooling systems,

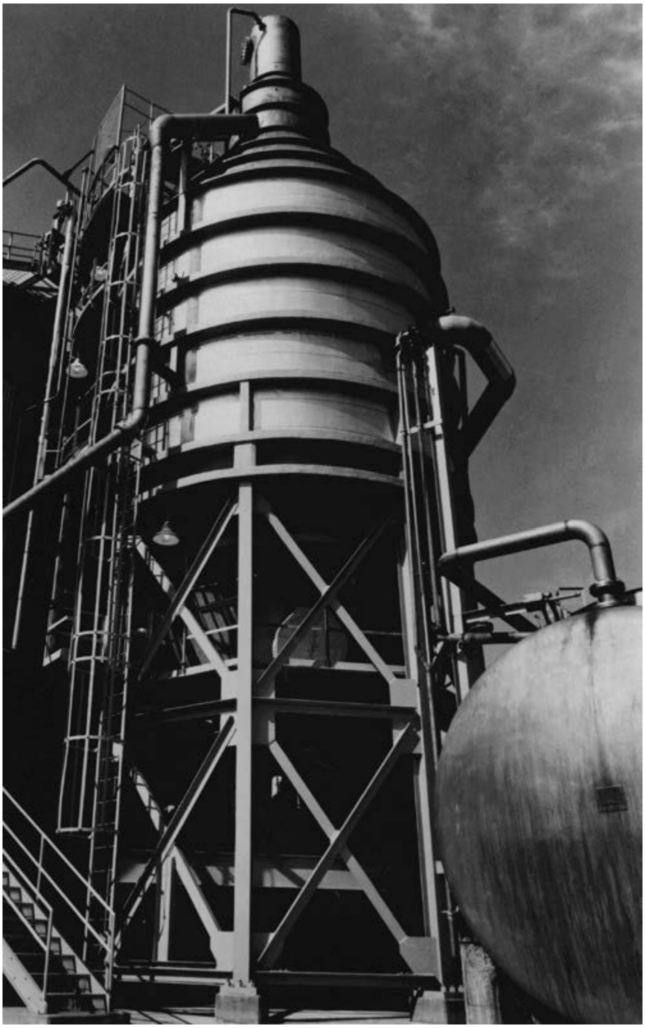

Figure 36.8 A large crystallizer producing ammonium sulfate. (*Courtesy of Whiting Corporation*.)

steam generators, and other special applications, to perform at a reasonable maintenance cost. Without these less expensive pretreatment chemicals, the increased use of the more expensive specialty chemicals would not be cost-effective. The following brief look at the processes used for the manufacture of some of these chemicals, introduces the chemical industry to those not familiar with it.

Some of the processes in the chemical industry seem more mechanical in nature than chemical. For example, nitrogen and oxygen are produced from air by a combination of compression, distillation, and refrigeration. Solutions such as brine or even water are evaporated, sometimes in solar evaporation ponds, to produce salt.

Other simple processes used in heavy chemical manufacture depend on a phase change. Native sulfur is melted underground by hot water and brought to the surface in molten form. Salt and sodium carbonate are dissolved and brought from underground strata to the surface in solution form.

Simple processes that rely on combustion include:

Sulfuric acid—Sulfur is burned over a catalyst to produce sulfur trioxide (SO_3), and this is dissolved in sulfuric acid (H_2SO_4) and concentrated to market strength by recycle.

Lime—Limestone is heated in a kiln, producing quicklime (CaO), which is converted to hydrated lime [$Ca(OH)_2$] by slaking with water. By-product carbon dioxide (CO_2) may be recovered from the kiln gases.

Phosphoric acid—In one process, phosphorus is burned to phosphorus pentoxide (P_2O_5) and dissolved in water. Sodium orthophosphates are produced by neutralizing this acid with sodium hydroxide (NaOH).

The major water treatment chemicals manufactured electrically, sodium hydroxide and chlorine, are made by electrolysis of sodium chloride (NaCl) brine, producing sodium at the cathode and chlorine at the anode. The sodium is then reacted with water to yield sodium hydroxide. Since they are coproducts, the price of one is affected by the market and price of the other. Chlorine and sodium hydroxide are used in many products and processes such as PVC, pharmaceuticals, nylon, paint, herbicides, adhesives, and catalysts. Most of the chlorine produced is used for manufacturing vinyl chloride monomer (VCM). Chlor-alkali plants are typically positioned close to VCM manufacturers and other chlorine derivatives.

Some heavy water treatment chemicals are byproducts or waste products. Ferric chloride, a coagulant, is a byproduct of the manufacture of titanium dioxide (TiO_2) and a waste product from hydrochloric acid (HCl) pickling of steel plate in a steel mill; hydrated lime is available in some areas as a byproduct of acetylene manufacture; hydrochloric acid is often a byproduct of the chlorination of organic compounds.

Alum (hydrated aluminum sulfate) is one of the water treatment chemicals produced in a multistage operation. The process flow sheet is shown in Fig. 36.9. In the preparation of raw materials, the bauxite is crushed and ground in the dry form and fed into the first reaction vessel, where it meets concentrated sulfuric acid and is diluted with washings from later operations. The mixture is heated with steam so that the reaction can take place rapidly; iron is removed as an impurity; and the liquor is fed to a clarifier, where a flocculant is added. The underflow solids are pumped to a two-stage washing system, where the alum liquor is recovered by having these solids washed with the condensate. The overflow is further concentrated in an open

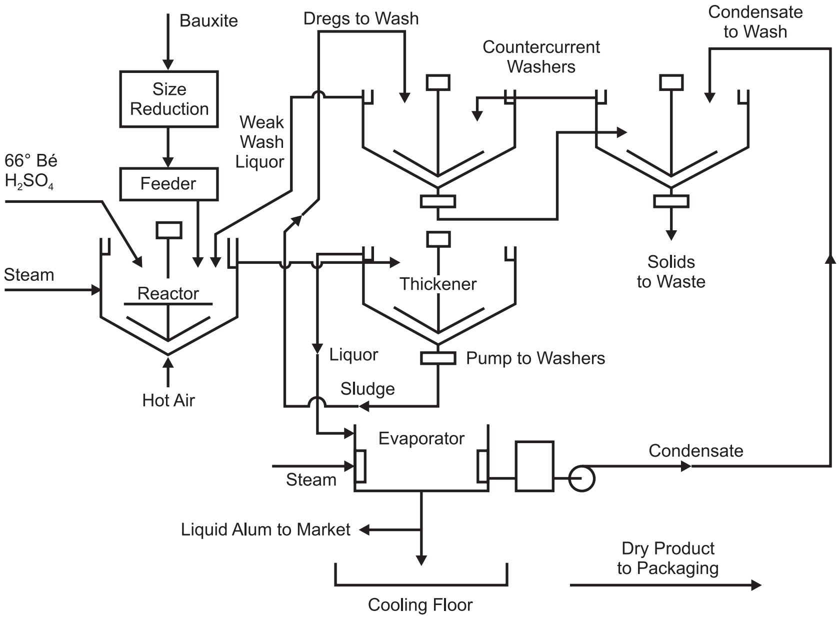

Figure 36.9 Simplified flow sheet of alum manufacture using several unit processes.

evaporator, and the concentrate is then discharged onto a cooling floor, where crystallization occurs. As seen in this flow sheet, the reaction takes place in relatively simple and compact vessels, and the balance of the equipment is for preparing the raw materials and finishing the product to meet the required specifications. Steam is required for the operation, and the condensate produced is used as the wash water in processing the waste solids.

Beyond the confines of water treatment chemicals, a good example of the complexity of the petrochemical industry is the manufacture of synthetic rubber, illustrated in Fig. 36.10. The raw materials are intermediates or specialty chemicals; the equipment for carrying out the reaction is quite complex; and the final processing steps are equally complicated. There is extensive use of steam and water throughout the process.

Ammonia and Fertilizers

Several factors have influenced the growth in demand for nitrogen-based fertilizer products. Population growth and global dietary changes, combined with a corresponding decrease in arable land (Fig. 36.11), require increasing yields from available agriculture through the use of fertilizers. Additional factors affecting demand for nitrogen products include mandated use of urea solution to reduce nitrous oxide emissions from diesel engines, and anticipated expansion of ethanol from corn.

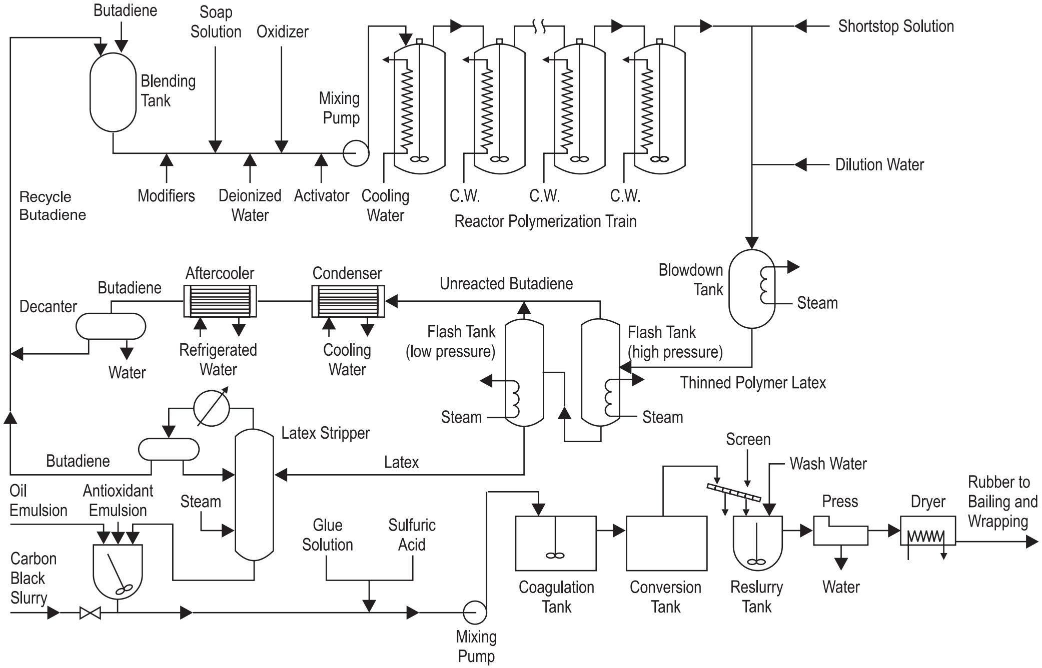

FIGURE 36.10 In petrochemical processes, a large variety of sophisticated units may be required, as in the manufacture of synthetic rubber. (*From Chemical Engineering, February 22, 1960, pages 121–126*.)

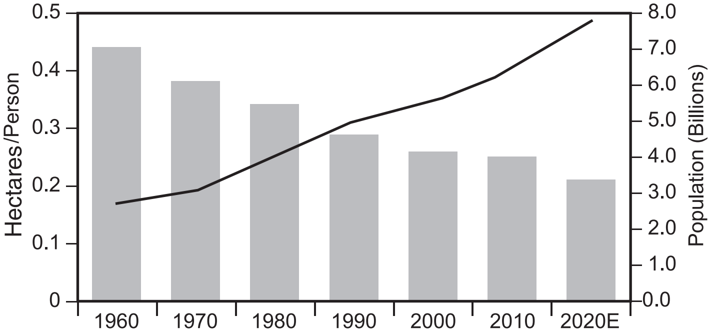

Figure 36.11 Arable land versus population. (*Compiled utilizing information from Potash Corporation, http://www.potashcorp.com/.*)

Nearly, all ammonia currently is produced by the Haber–Bosch steam reforming process. In areas where methane (natural gas) is available, hydrogen is separated out from the gas feedstock with steam in the presence of a catalyst. If natural gas is not an available feedstock, hydrogen is usually supplied by gasification of coal or coke. Nitrogen is drawn from the atmosphere via air compressor prior to adsorption in the presence of a catalyst. The process is outlined in Fig. 36.12.

Ammonia is the basic building block for a number of derivatives, such as urea, ammonium nitrate, nitric acid, and urea ammonium nitrate (UAN).

Efficient use of water for steam generation and process cooling is essential to the production of ammonia and upgraded products. Most plants produce high pressure steam requiring excellent purity of makeup water and reused condensate. In addition, proper treatment of cooling water is in order to maximize heat transfer in critical heat exchangers and surface condensers. Insufficient attention to water treatment may adversely affect overall plant efficiency due to inadequate process cooling, or negative effects on plant equipment such as gas compressors and the like. Fouling or scaling of heat exchangers may negatively impact plant production rates, shortening the time between major maintenance outages.

Environmental Effects

The problem of water pollution control is particularly complicated in the chemical industry. The flow charts have shown how widely water and steam are used in numerous operations, and each point of use represents a possibility for contamination with the raw material, intermediate, or finished product.

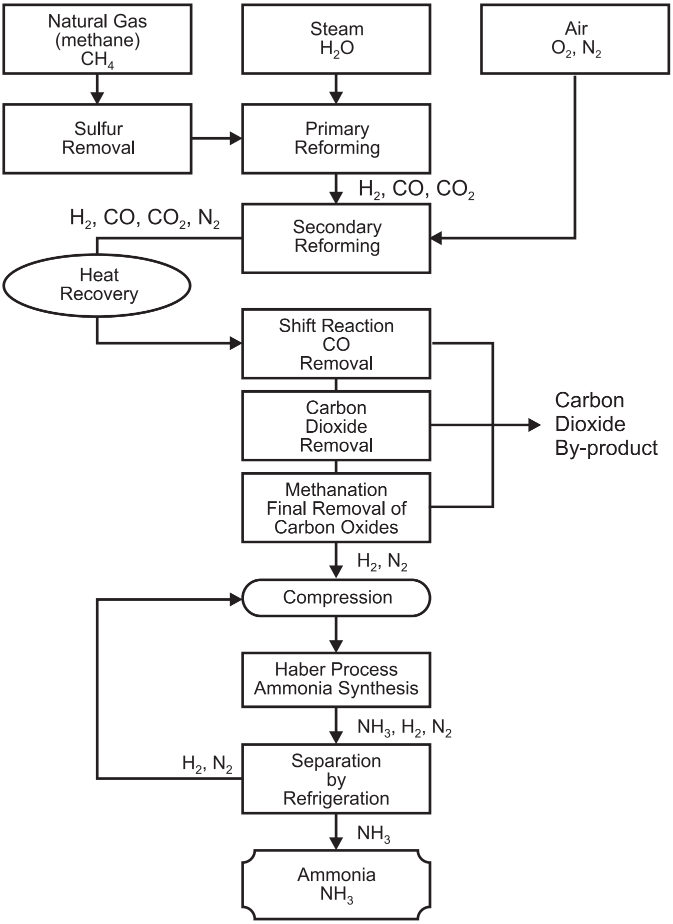

FIGURE 36.12 Haber–Bosch steam reforming process for producing ammonia.

It is usually less expensive to design the process to prevent contamination and to install equipment to recycle and recover chemicals, than it is to remove or neutralize the contamination after the fact in a waste treatment plant. For example, if the waste solids produced in the alum process (Fig. 36.9) still contain too much liquor to be acceptable in a landfill, a third washing stage may be added. In the removal of unreacted raw materials from a finished liquid organic compound, the installation of additional trays in the distillation column to recover the unreacted material may be much more practical than permitting the material to be discharged as a vapor or condensed in a barometric condenser, either of which represents a pollution problem.

Generally, if a chemical plant is producing inorganic chemicals, precipitation and separation equipment are usually used for the waste treatment operation. If handling organic chemicals, removal of organics by adsorption on activated carbon or by digestion in an activated sludge system is usually required. The organic residues present a difficult problem in that many of them are not easily digested by bacteria, and sometimes a combination of bacterial digestion plus activated carbon adsorption is required.

Table 36.3 lists a few organic compounds found in wastes from chemical plants. For the organic acids and alcohols shown on this list,

Chemical	BOD*	COD†	TOD‡
Acids			
Acetic	0.34–0.88	1.01	1.07
Benzoic	1.37	1.95	1.97
Formic	0.15–0.27	–	0.35
Maleic	0.38	0.83	0.83
Alcohols			
n-Amyl alcohol	1.6	–	2.72
n-Butyl alcohol	1.5–2.0	1.9	2.59
Ethyl alcohol	1.0–1.5	2.0	2.1
Methyl alcohol	0.6–1.1	1.5	1.6
Phenol	1.6	–	2.4
Isopropyl alcohol	1.45	1.61	2.4
Aldehydes			
Formaldehyde	0.6–1.07	1.06	1.07
Furfural	0.77	–	1.66
Ketones			
Acetone	0.5–1.0	1.12	2.2
Ether			
Ethyl ether	0.03	–	2.59
Cyclic Compounds			
Aniline	1.5	–	3.09
Benzene	0	0.25	3.07
Monochlorobenzene	0.03	0.41	2.06
Toluene	0	0.7	3.13
Xylene	0	–	3.16

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*Biochemical oxygen demand

†Chemical oxygen demand

‡Theoretical oxygen demand

TABLE 36.3 Waste Profiles of Selected Organics in Water (g O_2/g chemical) the biochemical oxygen demand (BOD) is usually over 50% of the chemical oxygen demand (COD) or the theoretical oxygen demand (TOD), and such wastes are amenable to biological digestion in an activated sludge system. Benzene and its close relatives are usually impervious to biological attack, and must be removed by stripping, adsorption, or both. Therefore, in many organic chemical plants, if a wide variety of compounds across the spectrum of active groups is present, the waste may require both biological and activated carbon treatments.

In any case, the pollution control engineer must be aware of all raw materials, intermediates, and finished products produced, recognizing that they may be found in the effluent. He should be familiar with the toxicological properties and tolerance levels of each, and their potential effect on the receiving stream, the waste treatment plant, the land surface, and subsurface aquifers. Pollution control in the chemical industry is unique in that the industry is responsible not only for its own wastes, but also for the ultimate fate in the environment of products it sells to others. One of the most difficult problems is monitoring the end use of containers in which products are supplied to customers.

CHAPTER 37

The Aluminum Industry

Aluminum is the most common metallic element in the earth's crust, comprising about 7.3% expressed in the elemental form (Al) or about 15% in the commonly occurring oxide form (Al_2O_3). Unlike iron, the next most common element, aluminum was unknown to the ancients, and it was only a century ago that the metal became available in commercial quantity.

As indicated by its position in the electromotive series, aluminum is a reactive metal. Because of this, reduction in aluminum oxide by carbon in a furnace, a process that easily produces iron from its ore, is unsuccessful because the aluminum metal produced is vaporized and quickly returns to the oxide form, when the reaction is reversed on cooling. Success in producing aluminum from the oxide was finally achieved in 1889 by the discovery of a unique electrochemical process. Hall in the United States and Heroult in France discovered the process simultaneously.

Aluminum manufacture has four distinct phases of production from raw ore to finished products: mining, bauxite refining, reduction, and fabrication. Another category is secondary production by independent scrap reclamation plants, but this is similar to recovery operations in the remelt section of the fabrication plant.

Mining

Bauxite is the ore used in the production of aluminum. It is a mixture of aluminum oxide trihydrate and monohydrate, with iron oxides, aluminum silicates, and titanium oxide impurities. The ore usually contains 5 to 25% moisture, which is removed from imported ores to reduce shipping weight and improve handling. In the United States, most ore is imported, but some Arkansas bauxite is processed. Lower grade aluminum minerals, such as kaolin and refuse from coal preparation, are being investigated in a variety of research programs attempting to extract alumina from such alternate sources.

Open pit mining accounts for almost all bauxite production. The overburden is stripped and the ore recovered by draglines and shovels. The ore is then sized and sent to the bauxite plant, where it is stored for blending and later use.

Bauxite Processing

To utilize the aluminum, the alumina in ores must be extracted and purified. This is done in alumina refineries, which produce a finished product of calcined alumina (Al_2O_3) necessary for the electrolytic reduction process, which is used to produce primary aluminum metal.

Of the nine basic alumina refineries operating in the United States, two are in Arkansas utilizing domestic bauxite. The others use ores imported from Australia, Jamaica, Africa, and other areas.

In an operation called the Bayer process, raw bauxite is digested by caustic solutions at temperatures as high as 475°F (246°C) and at pressures up to 500 psig (3.4 MPag), to yield a slurry containing sodium aluminate ($NaAlO_2$) and suspended waste solids called red mud. A process flow sheet is shown in Fig. 37.1. To allow efficient recovery and reduction in waste, the red mud is settled or filtered from the dissolved liquor, using natural and synthetic flocculants to produce a clear sodium aluminate solution.

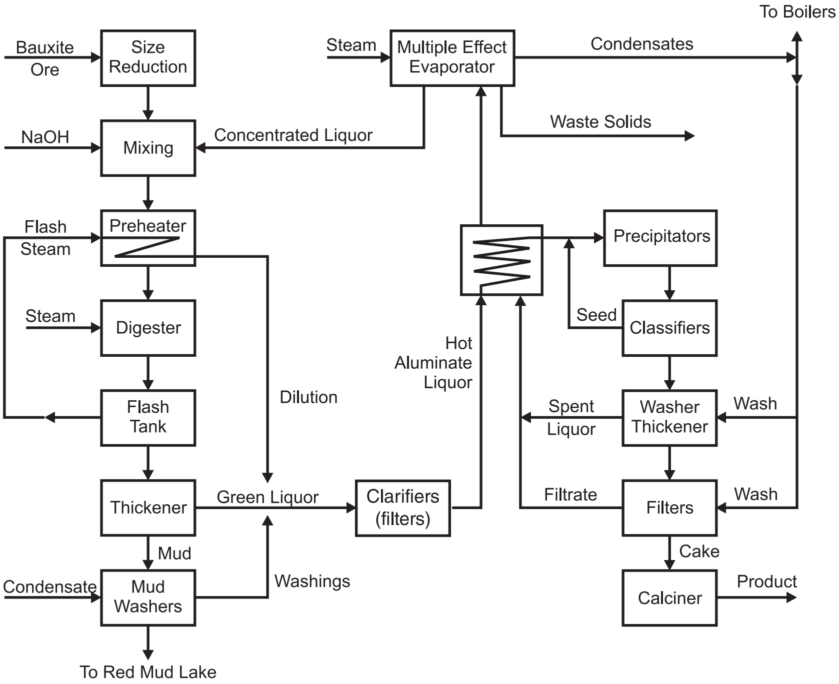

Figure 37.1 Simplified flow sheet of Bayer process for refining bauxite ore.

The red mud from the first separation step is reslurried with weak liquor in a washing operation to extract more of the aluminum and alkali. The most common practice uses a continuous counter-current decantation arrangement with as many as seven washing stages to recover almost all significant alumina and alkali. The red mud waste is finally discharged to a large mud lake (tailings pond).

After filtration, the pregnant liquor, rich in sodium aluminate, is cooled through heat exchangers to about 120 to 140°F (49–60°C) before entry into precipitation tanks. Here, seed crystals of previously precipitated alumina trihydrate are added and the tanks agitated for a day or two. This hydrolyzes the aluminate to yield aluminum trihydrate [aluminum hydroxide or $Al(OH)_3$], which grows on the seed material. This process is allowed to continue until about half of the alumina is converted. Further precipitation may result in excessive dropout of impurities, such as silica. The aluminum trihydrate slurry is then sent to classification and thickening tanks to separate the trihydrate from the spent liquor. The trihydrate is filtered and calcined to produce anhydrous alumina. Following the removal of the trihydrate crystals, spent liquor is concentrated by evaporators and returned to the beginning of the circuit.

Many Uses for Water

Water enters the process stream primarily as steam or condensate. A small amount of water may be introduced as purified makeup to prepare process reagents, such as flocculants or cleaning solutions. Storm water and waste surface water may enter the process as return water from the mud lake. Noncontact cooling water is used for equipment cooling and finished alumina product cooling. This water may be from an outside source or from the mud lake reservoir (Fig. 37.2).

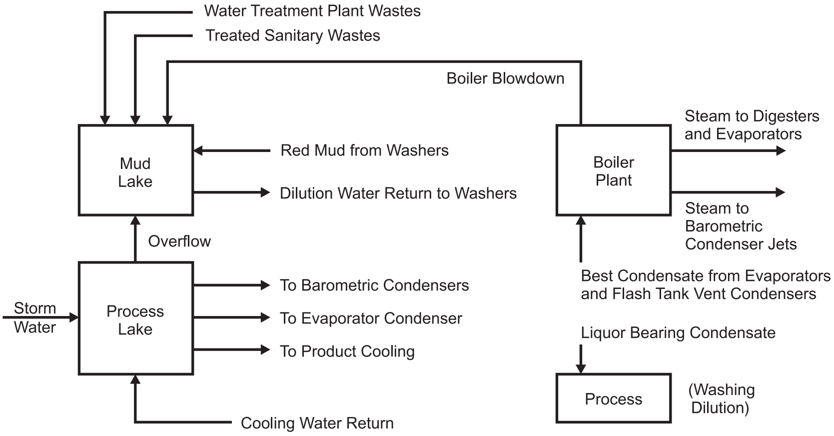

FIGURE 37.2 Water and steam uses in Bayer process.

Once in the process stream, water is used repeatedly as a solvent, to transport heat or slurry, wash away impurities, create vacuum, generate electricity, and prepare chemical makeup solutions.

A major input of steam comes from the digestion tanks, where the alumina is dissolved from the ore. As pressure is relieved in flash tanks, the lower pressure steam is liberated with its heating potential. This is used to heat the spent liquor before it joins the fresh bauxite in the digester, thereby recycling heat in a closed loop. Other uses for the steam from the digester flash tanks are in the evaporators concentrating the spent liquor.

Wash water streams vary in composition, depending on the product purity required. Condensate is used to wash the precipitate on the trihydrate filters to remove residual impurities. This wash water or other condensate may be used to wash the thickened trihydrate before going to filtration dewatering. Excess condensate beyond that required in steam generation may be used in final red mud washing along with mud lake return water.

Mud lake return water consists of overflow from gravity thickening as well as storm water inflows. The amount varies depending on local conditions. The water contains a low concentration of alumina and caustic from mud leaching. This proceeds to the last mud thickener, where it washes mud underflow from the previous thickener. Increased in alumina and caustic content, it joins mud from the second previous washing, and so on through the circuit. As it progresses up through the wash train, alumina and caustic values increase correspondingly. Finally, it joins the partially cooled digester discharge, where the final increase in alumina content is achieved. This countercurrent decantation process is designed to provide economical recovery of as much alumina and alkali as possible.

In addition to its use as an effective solvent, water serves to transfer solids from unit to unit within the process. This includes not only bauxite slurry, but trihydrate and red mud as well. It also provides a medium for wet grinding of the bauxite ore to the proper particle size for digestion. The use of water as a means of contact cooling of the overhead vapors and barometric condensers allows both the extraction of needed condensate water and the concentration of process streams. Water use in these barometric condensers may reach 5000 to 10 000 gal/ton (21–42 m^3/tonne) of product.

Because of process economics, the bulk of the unit process contact effluent streams, becomes intermediate feed streams to the other units as described. Noncontact streams represent a loss of heat rather than chemicals, and heat is recovered wherever practical. Even though no significant discharges are planned, water may be lost from any of the following production areas:

- Drying and calcining
- Red mud (evaporation and seepage from lakes or contained as part of the in-place mud content)

- Evaporation of liquor streams
- Sand disposal
- Evaporation of wash down water streams

The complete water use scheme, including the Bayer process circuit, is shown in Fig. 37.2.

Aluminum Reduction

Alumina produced by the Bayer process previously described is dissolved in a molten bath composed chiefly of cryolite ($3NaF \cdot AlF_3$), to which is added fluorspar (CaF_2) and aluminum fluoride (AlF_3). The molten mixture is prepared in an electrolytic cell, called a pot, illustrated by Fig. 37.3. A series of carbon anodes project into the bath from above. The amorphous carbon pot lining, with metal collector bars embedded in it, serves as the cathode. The pot lining is encased in insulation and refractory brick surrounded by an outer steel shell. The exact reactions in the cell are not completely understood, but the important result is a reduction in the aluminum oxide by carbon, according to the following reactions:

$$Al_2O_3 + 3C \rightarrow 2Al + 3CO\uparrow \tag{37.1}$$

$$2Al_2O_3 + 3C \rightarrow 4Al + 3CO_2\uparrow \tag{37.2}$$

The oxidation occurring at the anode produces a mixture of about 25% carbon monoxide (CO) and 75% carbon dioxide (CO_2), and this

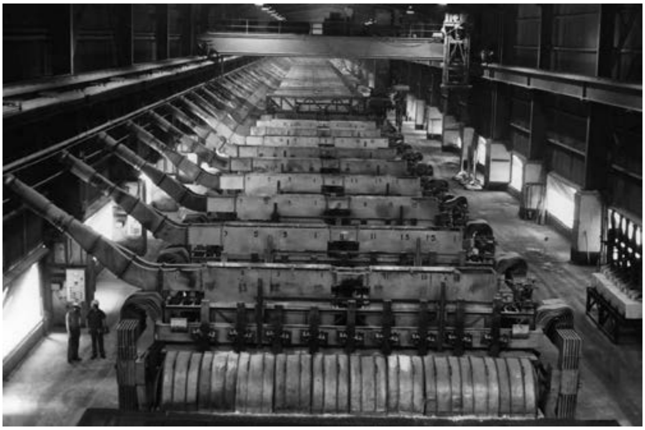

Figure 37.3 A pot line in an aluminum reduction plant. Fumes are withdrawn from each cell and delivered to a scrubber. Fresh anodes are in the rack at the right. The crane moves the tapping device and crucible from cell to cell. (*Courtesy of Kaiser Aluminum and Chemical Corporation*.)

exiting gas mixture carries with it certain volatile fluoride compounds. Carbon is consumed at the rate of about 0.5 lb per lb of aluminum produced (0.5 kg/kg). Aluminum is produced by reduction at the cathode, and a pool of aluminum metal collects on the bottom of the cell. The passage of current through the cell generates sufficient heat to keep the bath molten and at a temperature of about 1650 to 1740°F (900–950°C).

Frequent Feeding Necessary

The heat is contained by the insulation of the pot lining material, plus a crust, which forms on the surface of the bath. Although aluminum oxide is the basic raw material, it makes up less than 8% of the bath and must be continuously added. A supply of alumina is maintained on the crust, where it heats and dehydrates. The crust is broken periodically, and some of the alumina is stirred in to replenish what has been consumed by the reduction process.

Molten aluminum is periodically withdrawn (tapped) from the pot and cast into pigs or into any of the various types of ingots. The usual power consumption for aluminum reduction is in the range of 8 to 10 kWh per pound (18–22 kWh/kg) of aluminum produced, so that a pot line of perhaps 200 to 240 cells producing about 100 000 ton/year (91 000 tonne/year) of aluminum would have a power requirement of about 200 to 250 MW. Because of this high electric power requirement, aluminum reduction plants are usually located near low-cost sources of power. Typically, these plants use hydroelectric power or have contracted with nearby utility stations for a significant block of their electric output. Because direct current is needed for electrolytic cells, a substantial investment is required for electrical facilities to convert the alternating current available from public utilities to direct current.

Due to the high consumption of carbon electrodes, each plant has its own facilities for producing these from mixtures of petroleum coke and pitch. Rather extensive facilities are required for materials handling and processing of the electrodes. A flow sheet of an aluminum reduction plant and an electrode processing plant are shown in Fig. 37.4.

Exhaust Gases

In the reduction process, as indicated by the chemical equations shown earlier, consumption of the carbon electrodes produces a mixture of carbon monoxide and carbon dioxide. These gases leave the cell and carry with them certain volatile components from the bath, including fluoride compounds. Particulates from the surface of the pot are also entrained with the escaping gases. To control air emissions, hoods are positioned over each cell, and suction is applied to collect the gases. The gases are routed through wet scrubbers to

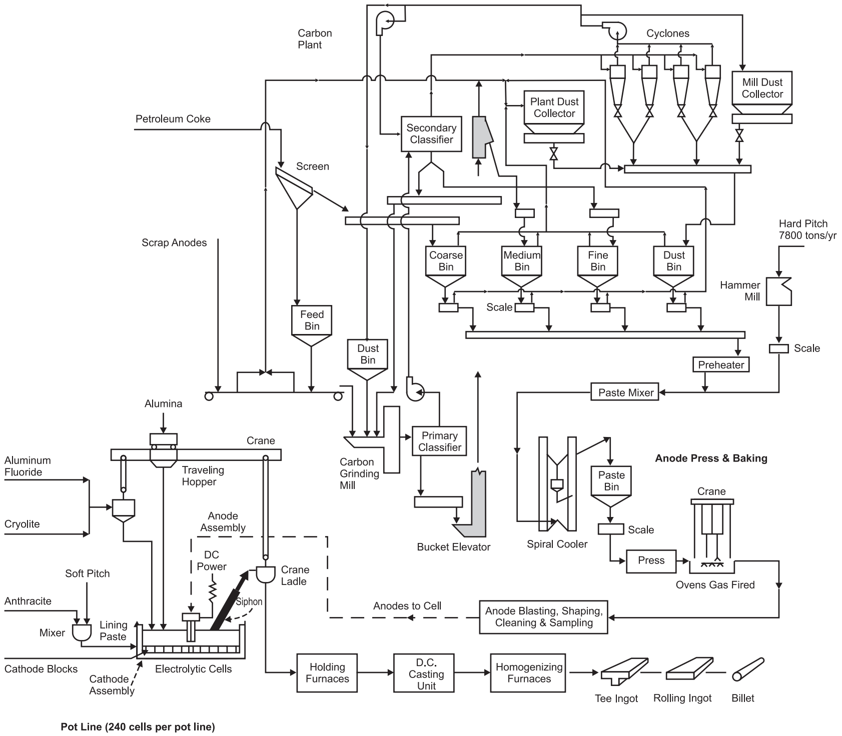

FIGURE 37.4 Flow sheet of aluminum reduction plant and electrode processing plant.

remove both gaseous and particulate materials. Since the fluoride content of the gas stream is valuable, the scrubbing water is often fortified with reactive chemicals, such as sodium aluminate, to produce various mixtures of sodium and aluminum fluorides. These can be returned to the bath after concentration and drying.

For air emission control in the electrode processing plant, wet scrubbers are sometimes used, and the scrubber water becomes a significant part of the total waste treatment load. However, it is more common to control these emissions with dry collectors.

Following the reduction in aluminum in the pot line, the metal is cast either by a continuous casting process, such as a small ingot casting machine, or by conventional casting into cast iron sow molds on a casting floor. In continuous casting units, spray water is used for external mold cooling. In a roll caster, water is used to cool the molds internally and as a spray to cool belts. The need for water of consistent quality and temperature is much more important for semi-continuous casting operations [Direct Chill (DC) and Horizontal Direct Chill (HDC)], than for conventional small ingot and sow operations.

The semi-continuous casting operations typically produce cast metal in the shape of rectangular ingots and cylinders called billets. In this operation, water is critical because it is contacting the finished shape and is thus part of the process. To cast these shapes utilizing sophisticated aluminum casting molds requires water providing optimized heat extraction, that is, quenchability. The cooling water is normally recirculated over evaporative cooling towers to remove heat from the process and to provide consistent year-round cooling water temperature. The systems can be difficult to operate because the water often is contaminated by casting lubricants, hydraulic oil, and plant cleaning materials. These materials provide food for microbes, making it difficult to keep the cooling system free of microbial masses. Precise chemical control of these cooling systems is necessary to optimize quenchability, while meeting the stringent plant environmental permits.

After casting, ingots are cooled by air or water spray. In some cases, the system is designed to produce a very fine spray so that the water evaporates completely to dryness, and leaves no residual wastewater for subsequent treatment. If an excess of water is required, it contains suspended solids and oil, and requires treatment before disposal. Air-cooling, either alone or combined with a water spray, will undoubtedly find increasing use as a way of minimizing wastewater discharge.

There are various other cooling water applications in the reduction plant. These include water for cooling hydraulic oil, green anodes, and compressors. The plant receives electric power from a nearby utility at high voltage, which must be reduced through transformers. The alternating current, at reduced voltage, is then converted by mercury arc rectifiers to the usable direct current. With the cells of the pot line being connected in series, this may be as high as 800 V, based on a loss of about 5 V at each pot. Cooling water is required for components of the rectifier.

There is a transformer and rectifier unit for each pot line. Cooling water may also be required for the chlorine compressors, which are used to supply chlorine gas for degassing molten aluminum.

The cast metal shapes produced in the reduction process proceed to further manufacturing facilities, where they are remelted and fabricated into finished products or extruded into structural shapes.

Metal Fabrication

The primary aluminum shapes produced in the reduction plants are remelted and converted into a wide variety of forms, including sheet, plate, structural shapes, rods and other bar stock, tubes, wire, and foil at various fabricating plants. Aluminum scrap is melted in reverberatory furnaces in operations quite similar to these in the primary smelter itself, where scrap must be reclaimed from butt ends and clippings. The same semi-continuous casting operation is used. In these operations, the nature of the impurities is unknown, so fluxing agents are added to eliminate them. The contaminants are removed as dross from the surface of the molten metal after casting. Some of the billets can be extruded by heating the metal to a temperature at which it becomes plastic, but the bulk of production is done in the rolling mill. Since initial rolling is done on hot metal, the hot ingot slabs may be sent directly to the rolling mill, but it is usually passed through furnaces to make certain that the temperature is uniform throughout. Cooling water is applied at the rolls to maintain the proper temperature for rolling, and lubricating oils (called rolling oils) are often applied to the hot mill system to facilitate rolling. The rolling oils also prevent the development of surface imperfections, caused by the friction of working through the rolls. The roll cooling water is recirculate and the debris from the rolling operation settled, with facilities provided to reclaim the rolling oil wherever possible.

In addition to the cooling water used on rolls, water may be required for cooling furnace doors and for typical utilities operations, such as compressor jacket cooling and bearing cooling.

Some fabricated shapes may be finished by special chemical treatment, such as the anodizing of aluminum sheet or tube by chromic acid treatment. These finishing operations may generate wastes that require separate treatment before discharge to the final waste treatment plant.

Most reduction plants purchase power from utilities and have no need for high-pressure boilers. Power may be generated in the bauxite plants, where turbines exhaust into the steam line supplying the evaporators. However, in the reduction plants, low-pressure boilers are operated for space heating in the winter, coolant and lubricant heating, and for electrode paste heating. The water treatment systems for these operations are usually quite fundamental.

The aluminum industry is very environmentally sensitive, and there is a major effort to minimize aqueous wastes and to tightly control water usage.

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CHAPTER 38

The Steel Industry

Archeologists have used the terms Stone Age, Bronze Age, and Iron Age to delineate successive stages of civilization. During the Bronze Age, humans learned to use charcoal as a reducing agent, as well as a fuel, to convert mixed ores of copper and tin into molten bronze in clay furnaces. Iron ores were not so easily reduced, and the same process that yielded molten bronze from copper and tin minerals, produced instead a spongy mass when iron ores were processed. The metal smith had to learn to beat this mass into a solid, and in the process, most of the slag fell away, but some was retained in the iron to produce what is known as wrought iron. Eventually, metal workers learned how to reheat this mass in the forge, so that it dissolved some carbon from the charcoal and was thereby converted to steel. Such secrets were carefully guarded as they provided the balance of power in warfare and commercial trade.

It was not until the late Middle Ages that relatively large-scale production of iron was achieved with the development of the blast furnace. However, iron produced by the blast furnace (pig iron) contained high carbon content; it was excellent for casting into shapes in molds, but it was not malleable. Processes were developed to convert pig iron into wrought iron or steel that is more malleable, and today, over 50% of steel produced still follows the two-step process of blast furnace followed by the converter that burns carbon out of molten iron to produce steel.

However, in developing countries that have fossil fuel reserves, direct reduction processes are being developed that turn back the clock of history and produce “sponge iron.” This product is mixed with scrap steel, and the charge is melted in electric furnaces to produce steel. In the United States, “mini-mills” have sprung up to compete with large integrated steel mills, and their major source of raw material is steel scrap. Almost one-third of the world’s steel production now comes from these electric furnaces, creating a large demand for scrap steel. This has raised the price of scrap to the point that sponge iron

	gal/ton	m^3/tonne
Blast furnace	350	1.5
Basic oxygen furnace (BOF)	2100	8.8
Direct reduction	290	1.2
Electric arc furnace	250	1.0
Continuous casting	1000	4.2
Hot strip mill	3100	13

Table 38.1 Water Usage Rates by Steelmaking Process

[direct reduced iron (DRI)] is widely used in electric arc furnace charging, with the likelihood that DRI production and processes will continue to grow.

Water usage rates in a steel plant can vary widely from 150 to 6600 gal/ton (0.63–27.5 m^3/tonne) depending on the type of steel plant, water quality, environmental restrictions, cooling system design, and numerous other factors.

A summary of water consumption rates by major process is shown in Table 38.1. With the use of best available technologies (BAT), water consumption rates can be reduced to less than 240 gal/ton (< 1 m^3/tonne) in electric arc furnace steel plants (mini-mills) and to less than 1200 gal/ton (< 5 m^3/tonne) in large integrated steel works.

Blast Furnace Operations

The blast furnace is the heart of the iron-making process. Iron ore, coke, and limestone are charged by a skip car to the top of a furnace. Most furnaces range from 16 to 28 ft (4.9–8.5 m) in diameter and may be 100 ft (30 m) tall. Raw materials, fed in layers to the furnace are iron ore or pellets, coke, and limestone. In the lower portion of the furnace, hot blast air is injected through a series of circumferential openings called tuyères, at about 30 to 90 psig (207–621 kPag) and 1800 to 2000°F (982–1093°C). Air flows upward through the burden of raw materials in the furnace, and gas exits the furnace top at 5 to 30 psig (34–207 kPag).

Coke (carbon) reacts with magnetite (Fe_3O_4) and hematite (Fe_2O_3) in the furnace, releasing iron (Fe^0) and producing carbon monoxide (CO) and carbon dioxide (CO_2) gas. Iron sinks to the furnace hearth, where the original impurities in the charge combine with the lime, forming slag, which floats to the top of the iron. Gas leaving the top of the furnace carries fine dust, which is separated and recovered in collection equipment. The combustible exhaust is used in reheating stoves and in generating steam at boiler houses. Iron and slag are periodically tapped and collected in special railcars every 2 to 6 hours, depending on furnace conditions.

To keep this large furnace working efficiently, much of the equipment connected with the furnace uses cooling water at various points. Figure 38.1 illustrates the overall dimensions and general cooling water utilization for a typical blast furnace. This generalized drawing shows that the blast furnace may be constructed in two ways. In older furnaces, water sprays provide cooling water on the outer shell of the furnace, as illustrated on the left side; in more modern furnaces, as illustrated on the right side, the furnace contains copper plates, which have hollow passages for cooling water built into the furnace wall. The primary task of the cooling water in the stack and bosh is to prolong the life of refractory inside the furnace and extend overall campaign life of the blast furnace.

Where plates are used, these are generally connected vertically in a series of 4 to 7 plates with water flow of 15 to 50 gpm (3.4–11 m^3/h) in each series. Temperature rises 12 to 25°F (7–14°C) throughout the series. Cooling demand for the refractory decreases as height above the ground increases.

Figure 38.2 shows a hearth and bosh section of the blast furnace. The bosh area reaches the maximum furnace temperature, ranging up to 4000°F (2200°C). At this point, cooling requirements for the furnace are most critical. The bosh area can be cooled with sprays, copper plates, or staves, which are blocks of copper or cast iron containing cooling water passages. The hearth or lower section of the furnace is typically cooled with sprays or staves.

In the tuyère area, air preheated in stoves is blown into the furnace. The tuyères are copper-jacketed nozzles with cooling water in the jackets. Heat exchange rates are extremely high, and it is important that the cooling system be protected from fouling or plugging to maintain adequate flow rates and heat transfer.

The large valves controlling the flow of hot blast air from the stoves to the furnace, must also be cooled to prevent failure or jamming.

The basic problem of water quality for all of these systems is protection from corrosion, scale, and fouling from silt or microbiological growths. Any of these problems can quickly lead to equipment failures and lost productivity.

Exhaust Gas Treatment

Hot air blown through the furnace changes in composition and expands in volume. Exit gas velocity is high and entrains solids, principally burden fines of ore, coke, and limestone. This dirty gas passes through a dry dust collector, where a majority of the heavier solids is removed, and then proceeds to a wet scrubbing system. Scrubbing water and dirty gas collide in a venturi or orifice system, where almost

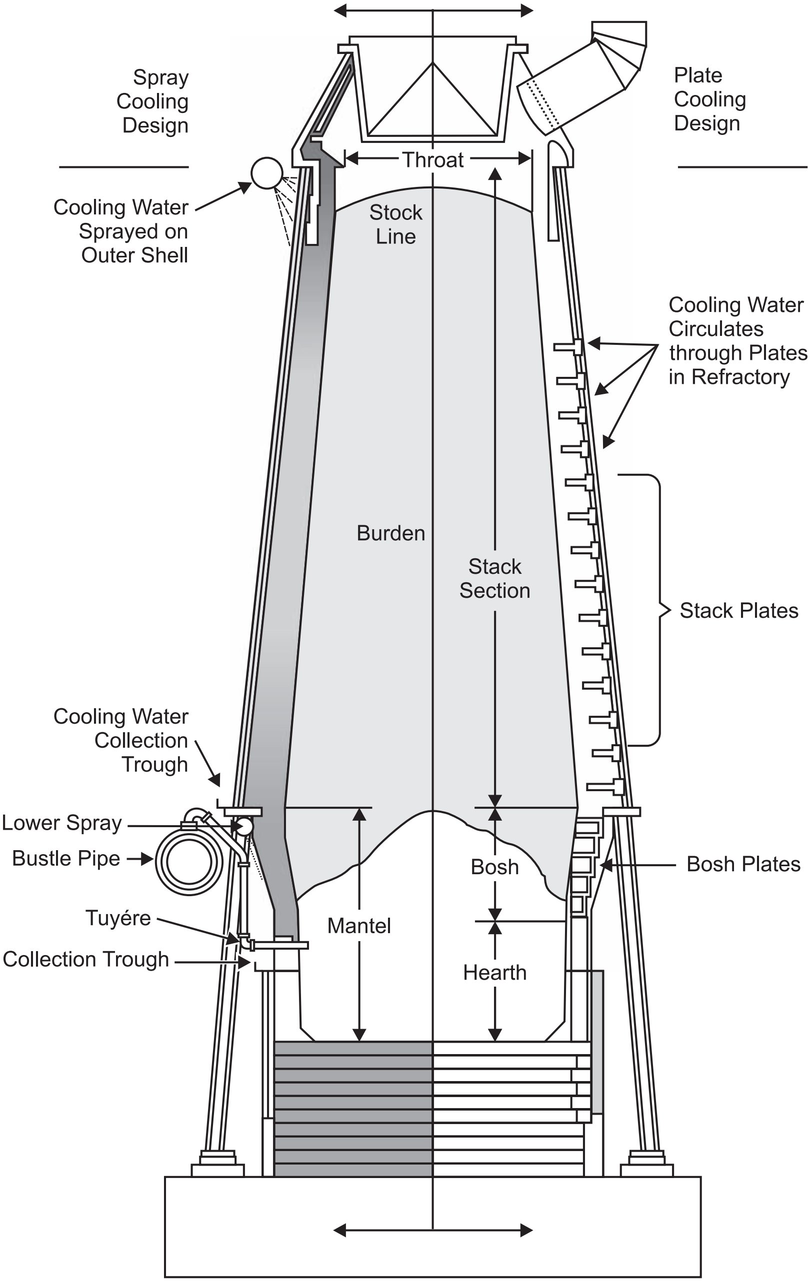

Figure 38.1 Blast furnace schematic showing two types of cooling water systems.

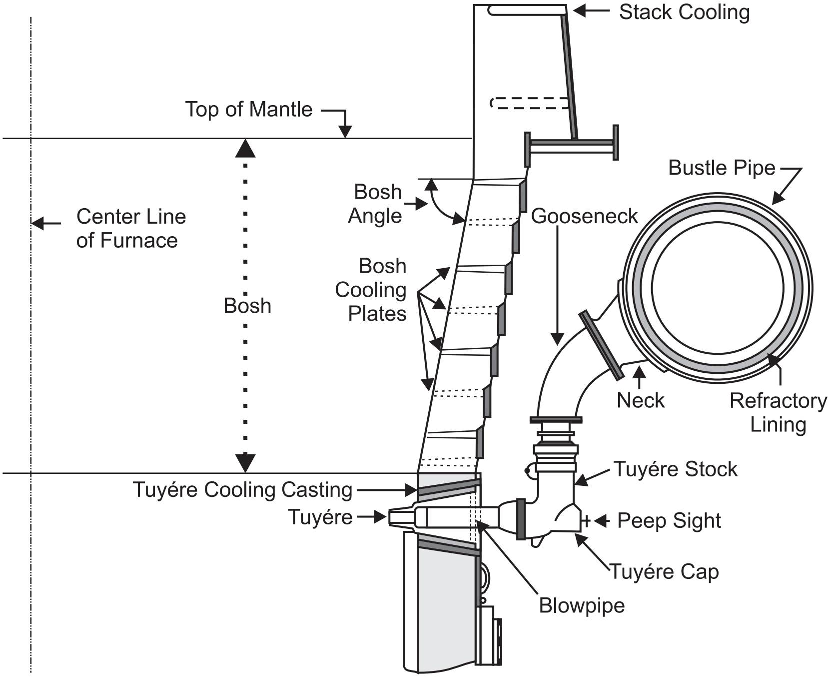

FIGURE 38.2 Blast furnace wind blowing area with plates for bosh cooling. (*Copyright 1971 by USS Corporation*.)

all suspended solids are removed (usually over 99%). The scrubbed gas contains 75 to 90 Btu per standard cubic foot (2.8–3.4 MJ/m^3) and is used for heating stoves or firing boiler house furnaces.

Scrubber water containing high suspended solids, from 500 to as high as 10 000 mg/L, is normally sent to a thickener or clarifier. Here, the solids are settled, and the effluent water is either discharged or recycled after appropriate treatment (Fig. 38.3).

The heaviest concentrations of solids settled from the water are normally iron, silica, and limestone. Soluble impurities usually include ammonia, phenols, and cyanide. Chemistry of scrubbing water continually varies as it is exposed to hot, dirty gas and then cooled and clarified before recycle. Cooling towers are often used to reduce temperature after the water contacts the hot gas. Evaporation of pure water vapor in the cooling tower concentrates dissolved solids within the water and affects its chemical balance. This must be considered when planning a proper cooling water program. Blowdown is required to control salinity of the recirculating water, and chemical treatment is needed for control of scale, deposition, and corrosion.

Additional water is used for slag granulation or for slag cooling. Where water is recycled within a slag pit area, there is usually a high

Figure 38.3 Clarifier-thickener used to treat blast furnace gas scrubber water and to recover solids. (*Courtesy of Inland Steel Company*.)

potential for deposition occurring within recycling lines and pumps. The water chemistry of these systems must be continually monitored.

There are a number of boiler houses in an integrated steel mill complex, and the boiler house in the blast furnace area is one of the most important. A major use for steam is to operate turbines, which drive large compressors delivering air to blast furnaces. A typical compressor discharges 100 000 scfm (2830 m^3/min) of air at 30 to 35 psig (207–241 kPag), requiring a steam turbine using about 350 000 lb/h (160 000 kg/h) steam at 900 psig (6.2 MPag). These turbines operate on a condensing cycle, but some low-pressure steam may be extracted for operation of auxiliaries, such as fans, pumps, and compressors in the utility area.

Steel Production

Steel is manufactured from iron (the blast furnace product) by three different methods: the basic oxygen process (BOP), the electric arc process, or the much older open-hearth process. The objective of each is to reduce impurities; for example, the 4% carbon content of the iron is reduced to about 0.2% in the steel product, depending on the metallurgical specifications of individual orders.

Basic Oxygen Process

In the BOP method, the mixture of hot metal from the blast furnace (usually 50–60% of the total charge), scrap steel, and slag conditioning materials, such as lime and fluorspar, are charged to the furnace (Fig. 38.4).

Figure 38.4 Hot metal is poured from the ladle into the tilted BOF as the first step in the steel making process. (*Courtesy of Baumco Gesellschaft fur Anlangenstechnik mbH, Essen, Germany*.)

Oxygen at a rate of 15000 to 20000 ft^3/min (425–566 m^3/min) is injected through a lance lowered into the vessel only inches (millimeters) above the raw materials. The oxygen blowing period continues for 20 to 25 minutes to melt and burn off or react out impurities.

A typical BOF vessel has 100 to 300 ton (91–270 tonne) capacity and produces steel in about 45 minutes. The vessel capacity is filled before the blowing of oxygen to allow space for the violent reactions to occur. In the quick basic oxygen process (Q-BOP) system, oxygen is blown through the bottom of the vessel, working through the materials and thus reducing the amount of violent splashing.

There are several water uses in the basic oxygen unit. First, the oxygen lance must be water-cooled. In most plants, this is a closed recirculating cooling water system. In most of these closed systems, lance water flows through the shell side of a heat exchanger, with cooling water on the tube side of the exchanger.

Because of the high heat release, gases leaving the furnace hood during the oxygen blow are very hot. The hood is usually cooled with water recirculating through the hood panels from both open and closed cooling circuits. A number of systems have boilers installed in the hood area for waste heat recovery and cooling of hot gases.

As gases leave the hood area, they can be further cooled by a wet scrubber and gas cooling system, which requires large volumes of water (Fig. 38.5). This water is then sent to clarifier–thickeners for sedimentation of solids, and water can be recycled or discharged. There is a wide swing in water composition through the entire heat, as shown by a pH record of the effluent from a gas scrubber. Those systems not using wet gas scrubbers normally have electrostatic precipitators.

Electric Arc Furnace Process

The second method of steel making is the electric arc furnace process (Fig. 38.6), which can produce the common grades of low-carbon steel or, by charging with alloying materials, special steels such as stainless or tool steels. Electric furnaces normally operate on scrap and have the advantage of being adaptable to almost any part of the country close to special markets. Since they are not dependent on the hot iron from a blast furnace for their production, they are not tied down to the traditional steel centers.

Most electric arc furnaces are equipped with water-cooled side panels or shells, roofs, off-gas elbows and ducts, electrode arms, cables, and clamps. While most electric furnace operations use baghouses to clean off gases, some plants use wet gas scrubbers.

Open-Hearth Process

The open-hearth process is the oldest of the steelmaking processes. In the open-hearth process (Fig. 38.7), the same basic materials used in the BOF process are charged to the open-hearth furnace. Hot metal is not as essential to the open hearth as to the basic oxygen unit. These furnaces normally produce 100 to 600 ton (91–540 tonne) of steel per heat over a period of 6 to 12 hours. In open-hearth furnaces, oxygen lance cooling is also required, similar to the BOF process.

The open-hearth process has been replaced with either the BOP or the electric arc furnace process in most steel plants around the world.

Direct Reduction Processes

As true of many developing technologies, a wide variety of processes is currently competing to determine which is best for the market of DRI. These processes are designed to handle a wide selection of

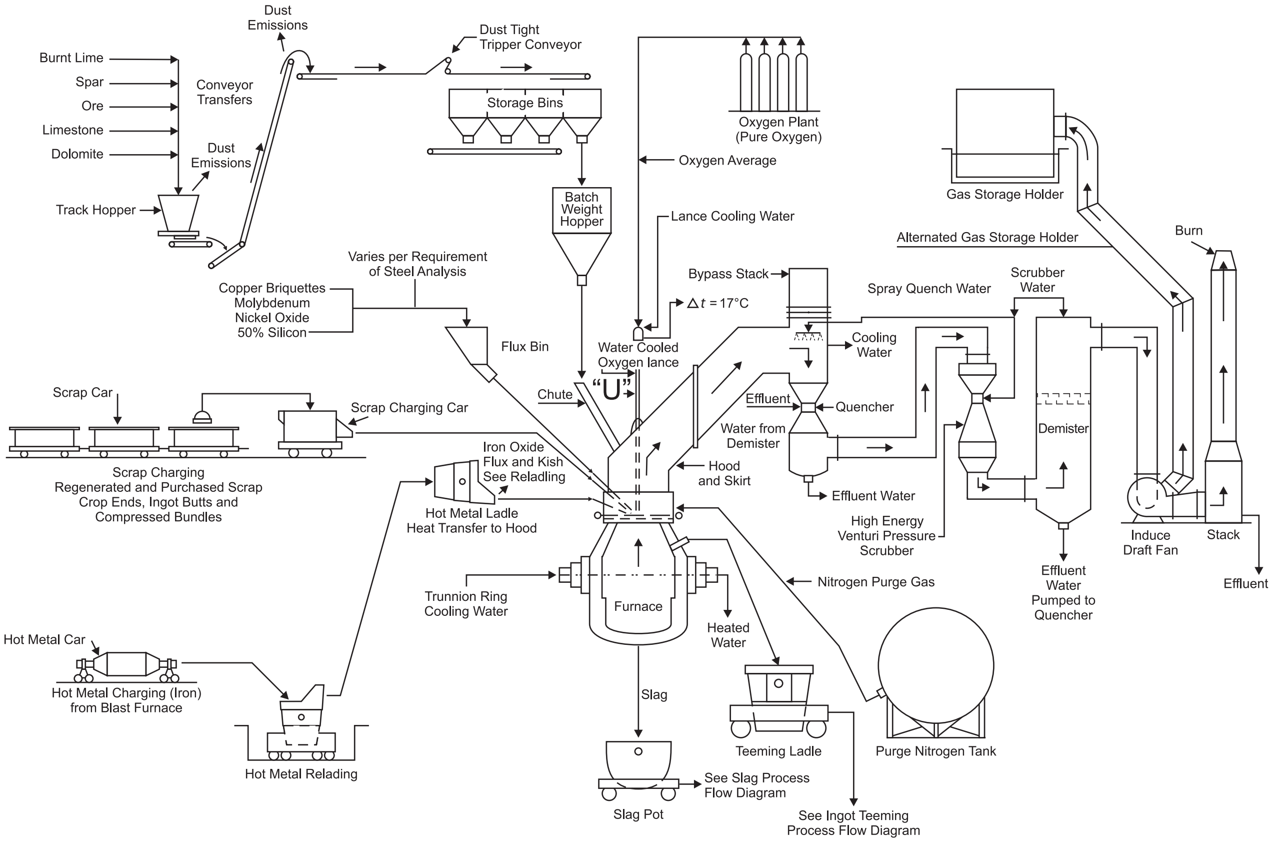

FIGURE 38.5 BOF showing major water uses for cooling and scrubbing. As different materials are added to the vessel during a heat, composition of scrubber water varies. (*From EPA 440/1-74-024a, "Development Document for Effluent Limitation Guidelines and New Source Performance Standards for the Steelmaking Segment of the Iron and Steel Manufacturing Point Source Category"*.)

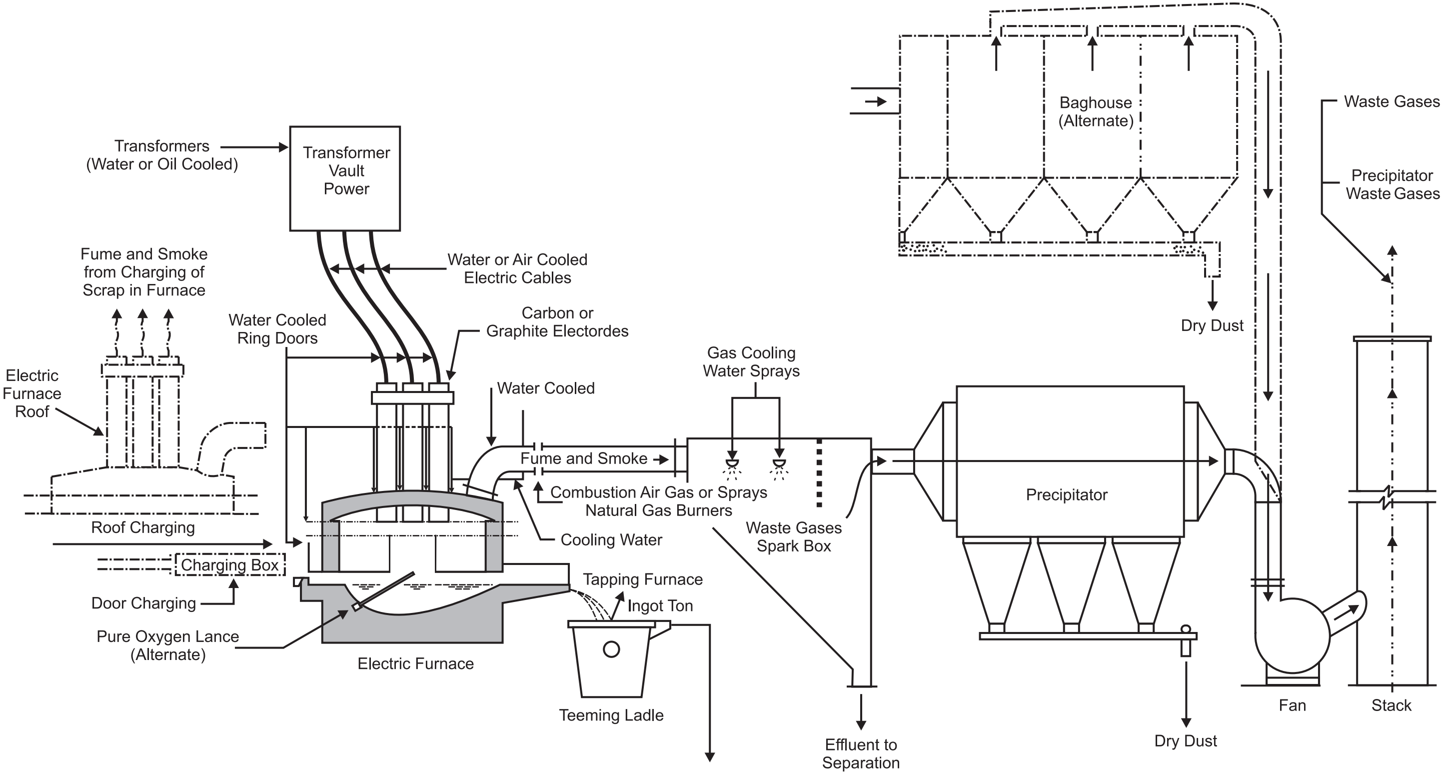

Figure 38.6 Electric furnace process for converting scrap to steel showing water circuits. (*Adapted from EPA 440/1-74-024a, "Development Document for Effluent Limitation Guidelines and New Source Performance Standards for the Steelmaking Segment of the Iron and Steel Manufacturing Point Source Category"*.)

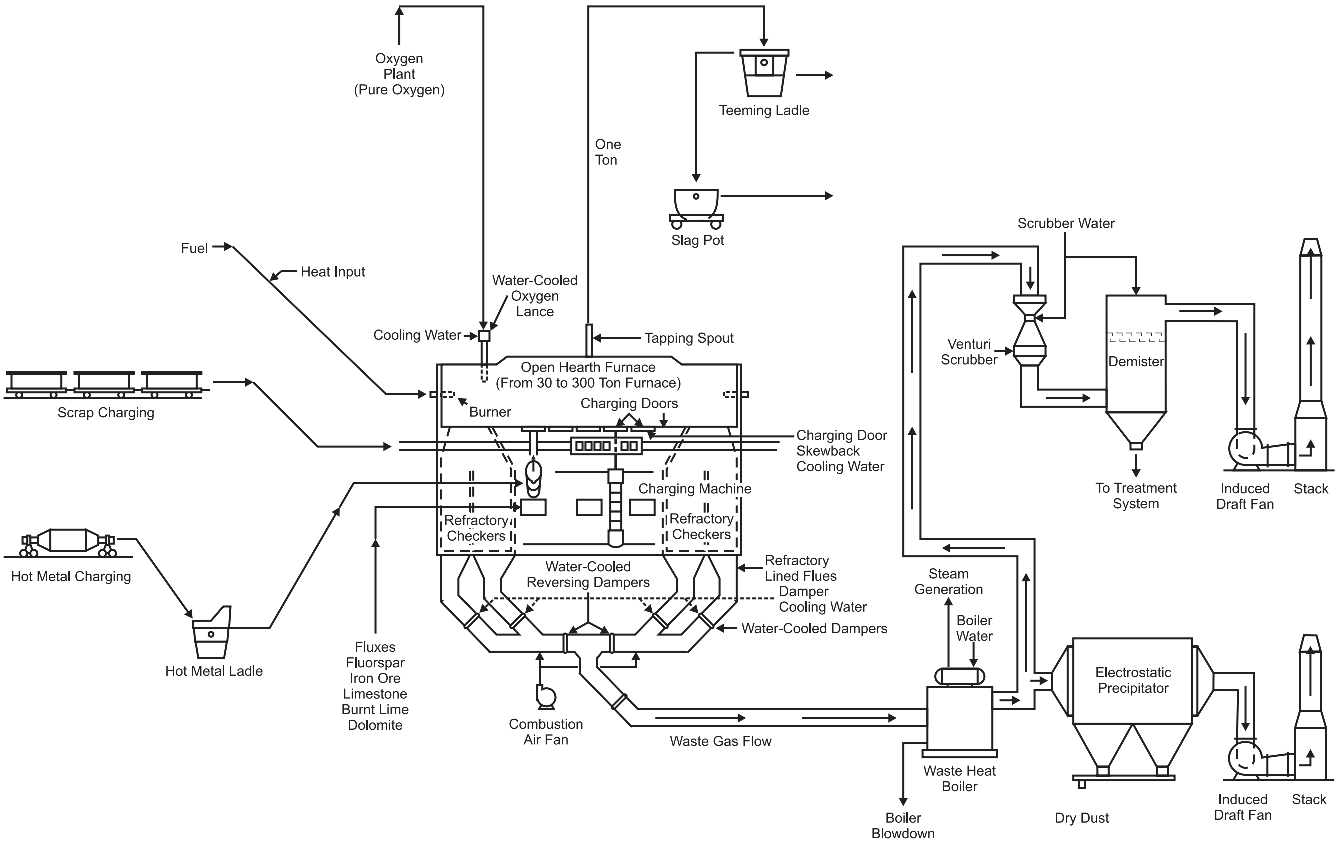

FIGURE 38.7 Open-hearth furnace operation showing water used for cooling and scrubbing. (*Adapted from EPA 440/1-74-024a, "Development Document for Effluent Limitation Guidelines and New Source Performance Standards for the Steelmaking Segment of the Iron and Steel Manufacturing Point Source Category"*.)

reducing agents from solids (coke, as used in the blast furnace, coal, and lignite) to liquids (oil) as well as gases (coke oven gas, reformed natural gas, and producer gas). The largest DRI production rates are from gas-fired furnaces. The charge may include solid reductant, with supplemental fuel sometimes added, plus iron ore or pellets, and limestone or dolomite as a sulfur-reducing agent.

There are two furnace designs:

1. The horizontal furnace is essentially a tilted kiln (like a lime or cement kiln) with air and fuel fired into the discharge end countercurrent to the flow of solids. Air distribution to the kiln is critical to good temperature control to avoid clinker formation and poor control of carbon content of the sponge iron. Coal can be used directly as a portion of the charge and as fuel, and this type of furnace favors coal-rich nations. However, production can be increased if the secondary fuel is oil or gas instead of coal.
2. The vertical shaft furnace has been designed for either fixed-bed or moving-bed operation. Reductant and fuel are usually both natural gas; however, coal can be a portion of the reductant, and coal can be converted to producer gas (coal gas), so indirectly coal could be used as both reductant and fuel.

Sponge iron discharged from the furnace can be crushed, screened, and separated magnetically from slag and char. The iron may be briquetted for easier transport and shipping, or go directly to a nearby electric furnace for charging.

Water is used for cooling in a number of operations, such as recycle gas cooling, product cooling or quenching, and machinery equipment cooling. Water is also used for gas scrubbing, and in the case of coal gas or reformer gas production, for steam generation.

Continuous Casting

Continuous casting (Fig. 38.8) was developed to reduce the overall cost of steel manufacturing by eliminating several steps in conventional steel preparation such as ingot teeming, soaking, and blooming. Continuous casting is the process of continuously pouring molten metal from a ladle into the complex casting equipment, which distributes the liquid, shapes it, cools it, and cuts it to the desired length. Casting is continuous as long as the ladle has available metal. Should one ladle follow another without interruption, the process is called “piggy-backing a cast.”

Correct water treatment and distribution are critical to continuous casting. Steel leaving the ladle at about 2800°F (1540°C) is poured into a tundish. The bottom of the tundish has one or more openings through which molten steel is distributed to form slabs or billets in

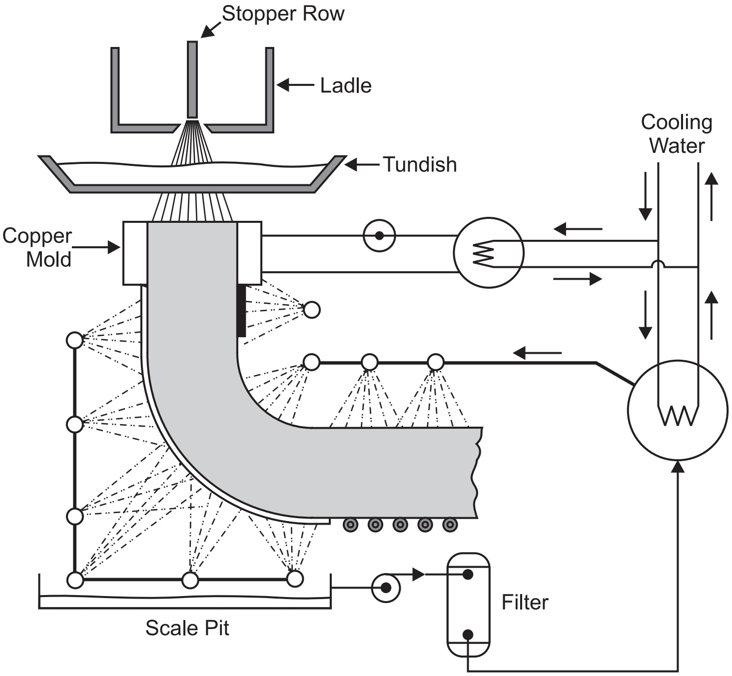

Figure 38.8 Continuous casting of slabs or billets.

the forming area called the mold, which is a water-cooled copper jacket providing ultra-high heat exchange rate. At the start of a cast, a dummy bar is moved close to the top of the mold to completely seal the interior. As the cast starts, this bar is slowly lowered to receive molten metal, and the cooling effect of the water-jacketed mold starts the formation of a metal shell. Proceeding through the length of the mold a distance of 30 to 36 inches (about 1 m), the dummy bar and shell-contained metal are exposed to a series of direct-contact water sprays, which help to complete the job of solidifying the steel. As solidification is completed, the dummy bar is cut from the formed metal and removed. The continuously moving, solidified billet or slab then moves through guides to the straightening rolls and onto the runoff table for cutting to desired length.

The crucial point in this process is the copper water-cooled mold, which forms the initial shell. Unless the shell is formed quickly and uniformly, a product defect or breakout can occur. A breakout of liquid steel occurring below the mold is very costly and hazardous. The most reliable cooling water program uses the highest quality water available in a closed loop with a secondary open cooling loop. Condensate, high-purity boiler feedwater, or low-hardness waters have been used as makeup. Hardness levels should never exceed 10 mg/L. Since the system is closed, there is little water loss, and the best corrosion inhibitors and dispersants can be used.

Spray water that contacts the billet or the slab becomes contaminated with iron oxide particles, as the hot metal is oxidized, along with oil and grease. The water is normally processed in a filtration system for solids removal, recirculated over a cooling tower, and then recycled back to the sprays, which must be kept from plugging at all times, because the flow of water to the billet or slab being cooled must be uniform at all points.

Auxiliary mechanical equipment of the continuous caster such as machine rolls, bearings, segments, frame, and torch cut-off equipment are also water-cooled. This may have a separate cooling water system, or it may be consolidated with the spray cooling water.

Hot Mill Rolling Operation

The hot mill (Fig. 38.9) produces such products as sheets, plates, bars, rods, and structural shapes. The first step in rolling is heating the steel billet or slab in a reheat furnace to as high as 2350°F (1290°C). Cooling water must be used to cool the doors, frames, and other components of the reheat furnace, and this may come from a closed or open recirculating cooling circuit. As the heated billet or slab leaves the furnace, high-pressure water [2000 psig (14 MPag)] and even higher is blasted onto the surface to remove oxide scale, so that no imperfections are caused by rolling this debris into the metal.

Water is used for roll cooling and for spraying directly onto the steel before being handled at the end of the mill. A high-speed sheet mill operates in the range of 4000 to 6000 ft/min (1220–1830 m/min);

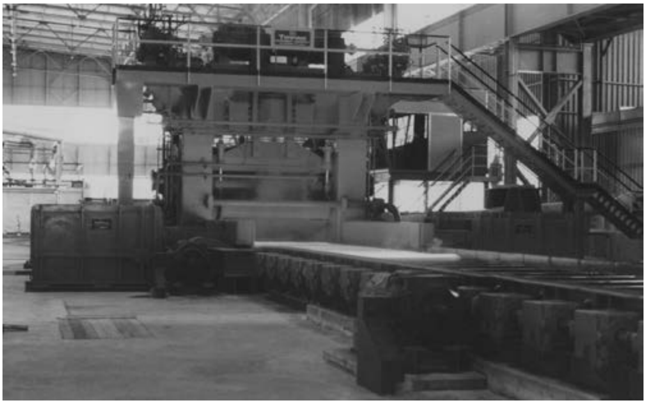

Figure 38.9 Hot mill rolling plate for further reduction through hot strip mill. (*Courtesy of Tippins Machinery Company, Inc.*)

a high-speed rod or wire mill operates at 8000 to 10000 ft/min (2440–3050 m/min). As water passes over hot metal from rolling station to rolling station, oxides washed from the metal are carried to a scale pit. There is a wide particle size range generated during descaling operations as the slab or billet travels through the mill. Larger particles are removed during initial rolling (the roughing end), and very fine particles are washed off in final rolling operations (the finishing end).

Much of the scale encountered in the scale pit can be removed with clam-type diggers, electromagnets, or traveling screen grates, but fine-sized particles are separated with coagulation in water clarification or filtration equipment. Most new plants recycle water used in the hot strip mill (Fig. 38.10).

When water is recycled through the mill, attention must be given to potential problems of scale, corrosion, fouling, and microbial activity. This is especially true for water going to the high-pressure pumps and sprays.

Considerable amounts of water are used for cooling electric motor systems in many of these mills. Motor-driven rolls keep the

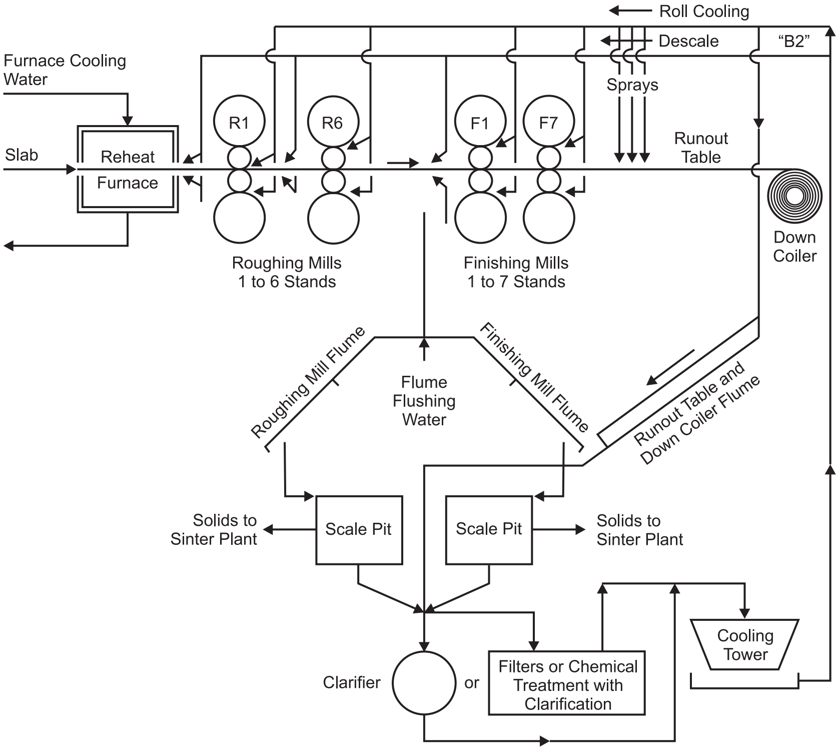

Figure 38.10 Hot strip mill showing recycle of clarified water for roll cooling and scale removal.

product moving to its end point. There can be as many as 300 to 400 motors at an installation.

Cold Rolling Mills

Cold rolling mills are divided into two categories: single stand and multistand, where steel is rolled in tandem. Because the steel is cold, it is hard to work, and the cold rolling process requires lubricant (soluble oil) in the water not only to cool but also to give a good finish to the steel. Water properties to be controlled in this operation include total suspended solids, iron, and oil. There are two systems for feeding lubricant and water in a cold rolling operation: recirculating and once through.

Recirculating System

In the recirculating system, a weak emulsion of oil and water circulates to the roll for cooling and lubrication of the sheet, collects under the roll, and then passes through to the treatment process. Emulsion is carried from the first stand to the second, third, and fourth. Spent liquid is normally collected, and an emulsion breaker is used to free the oil. Solids are settled and reclaimed for the iron content, and oil is reclaimed and reused (Fig. 38.11).

Water treatment for these systems consists of sedimentation, flocculation, filtration, and air flotation. Flows from these operations vary from 200 to 1500 gal/ton (0.83–6.3 m^3/tonne) of steel processed.

Once-Through System

Another cold rolling operation using direct application of oil is the once-through system, used on thin gauge material such as tin plate. The usual treatment system serves a multistand mill, having two to five stands. A 5 to 10% oil-in-water emulsion is applied to the steel at the first four stands, while a detergent solution is applied at the last stand. A once-through system is often used for this service, since the water must be kept extremely clean.

Wastewater, which contains a significant amount of oil, goes to a treatment system that includes an air flotation unit with oil skimmer, chemical treatment, aeration tanks, flocculating tank, and a settling basin or clarifier. Emulsion breaking chemicals may be required for efficient treatment of this waste. Oil is reclaimed and reused, while sludge is typically sent to a landfill.

Heat Treatment

To produce special physical properties in certain grades of steel, the metal passes through a series of heat treatment operations including heating in a furnace, annealing at a carefully controlled temperature for a specified period, quenching in water or oil, and final cooling in air.

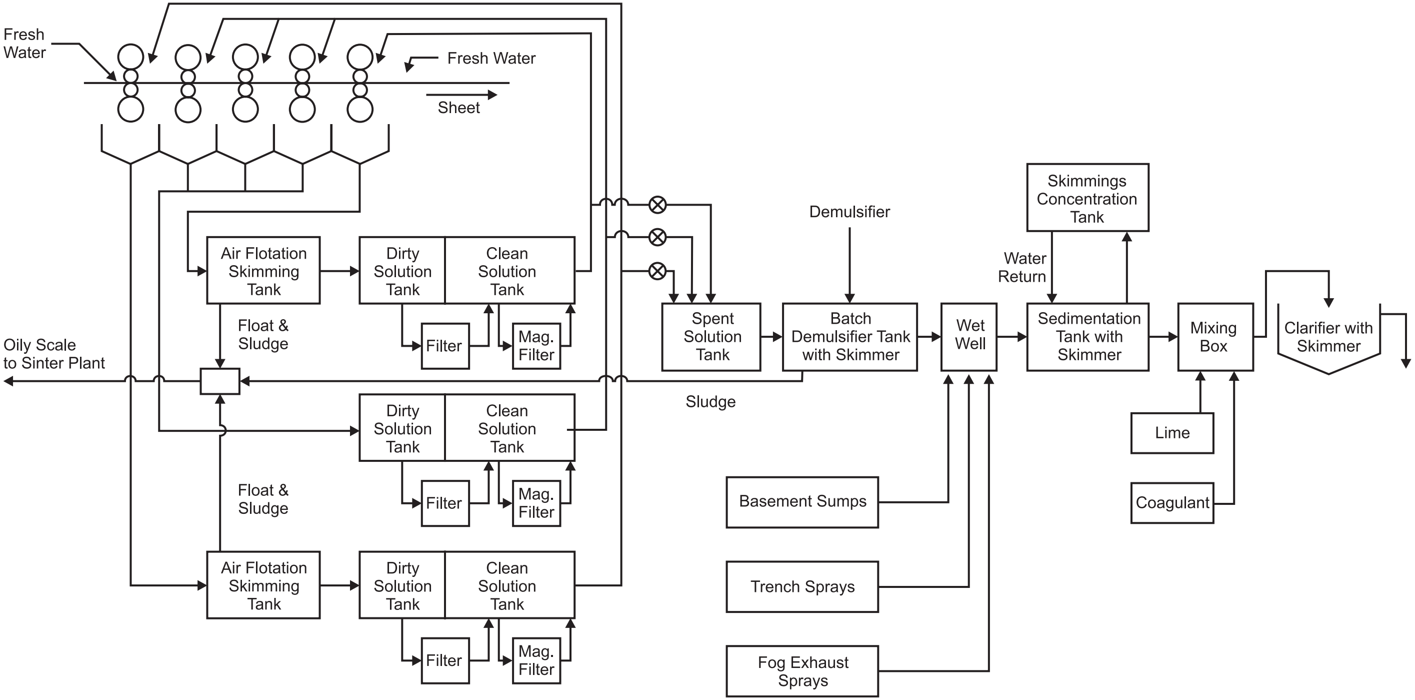

FIGURE 38.11 Cold rolling mill with recirculated water containing rolling oil emulsion. Provision is made for periodic treatment of spent rolling oil emulsions.

Generally, temperatures in annealing furnaces are not so high as to require water-cooling of furnace elements, but some cooling may be needed in special cases. Temperature of the quench oil or water quenching tank must be carefully controlled, and the coolant in the quench tank is usually recirculated through a heat exchanger to remove heat brought into the system from hot metal. Inadvertent discharge of oil, which could arise with overflowing of the quench oil tank, or by rupture of a tube in the oil–water heat exchanger, must be guarded against. Oil is generally the only likely contaminant in the heat treatment area.

Sintering

Sintering is a process that recovers valuable solid residues from scrubbers and clarifiers. This process includes collection of useful materials such as iron ore fines, mill scale, limestone, flue dust, and coke fines (Fig. 38.12).

The various materials are mixed in controlled proportions with a fixed amount of moisture, then distributed onto a permeable grate and passed through to a gas-fired furnace (ignition furnace). Combustion air is drawn downward through the bed. After a short ignition period, firing of the bed surface is discontinued, and a narrow combustion zone moves downward through the bed, with each layer in turn heating to 2200 to 2250°F (1200–1232°C). In advance of the combustion zone, moisture and volatiles vaporize. In the combustion zone, bonding of the particles occurs, and strong agglomerate is formed.

Most heat from the combustion zone is absorbed by drying, calcining, and preheating the lower layers of the bed. When the combustion zone reaches the base of the sinter mix, the process is complete. Sinter cake is tipped from the grate and broken up. After screening, undersized material is recycled, and the remaining sinter is sent to the blast furnace.

Water is added to the sinter mix to control moisture at 5 to 8%. Water is also sprayed for dust control in the plant and at the many conveyor transfer points, where raw materials are moved from storage areas to the sinter line (strand).

Many plants scrub sinter furnace exhaust gases to remove entrained solids. Scrubber water usually requires treatment by coagulation or flocculation to remove suspended solids. Additional chemical treatment may be required to control scale, corrosion, and fouling and removal of pollutants before discharge.

Acid Pickling

Treatment of steel in an acid bath, known as pickling (Fig. 38.13), removes oxides from the metal surface and produces a bright steel stripped down to bare metal and suitable for finishing operations,

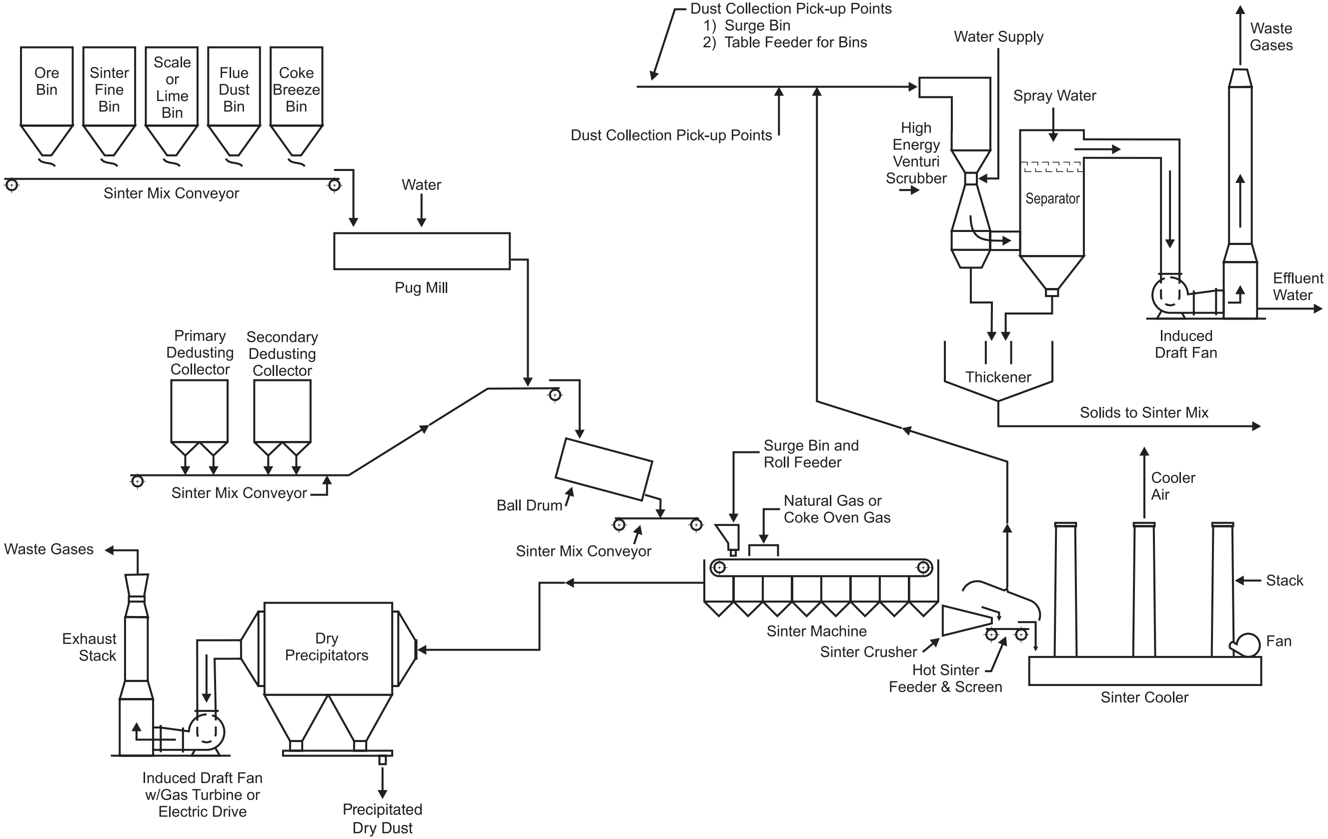

FIGURE 38.12 Sinter plant showing wet and dry dust collection. (*From EPA 440/1-74-024a, "Development Document for Effluent Limitation Guidelines and New Source Performance Standards for the Steelmaking Segment of the Iron and Steel Manufacturing Point Source Category"*.)

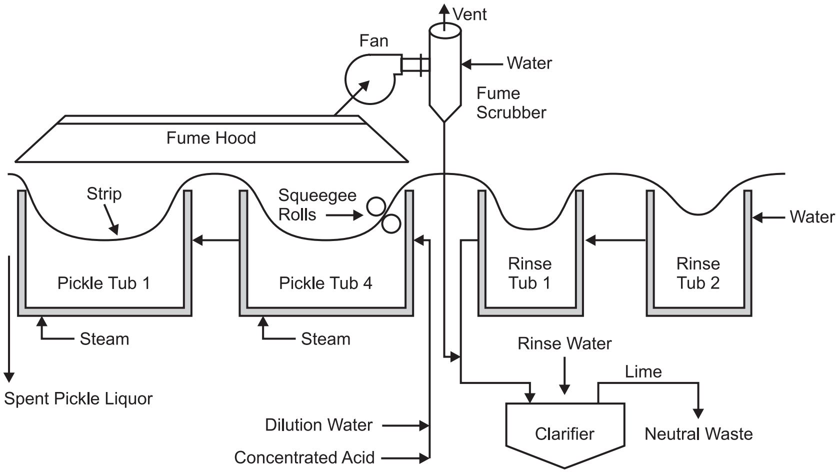

Figure 38.13 Acid pickling of steel sheet.

such as plating, galvanizing, or coating. Both sulfuric and hydrochloric acids are used, with the latter growing in popularity as more by-product hydrochloric acid becomes available from the chemical industry. With either acid, disposal of spent pickle liquor can be a serious problem.

Pickling may be either batch or continuous. Usually, acid is prepared at about 5 to 15% strength, depending on the work to be processed in the pickle tank and the type of acid used for pickling. As acid works on the oxide surface, there is gradual buildup of iron in the pickle solution and depletion of acid. When the iron content reaches a level that slows the pickling operation, the bath is either dumped or reprocessed. In some pickling operations, acid is continually withdrawn in order to hold a constant ratio of iron to free acid in the pickle bath, thereby maintaining uniform pickling conditions. Metal leaving the pickle bath carries some liquor with it into the subsequent rinsing and neutralizing operations. Loss of acid varies with the type of work, shape of the products being pickled, and speed of the operation. Appreciable rinse water must be added to the rinse tank and withdrawn continuously for discharge to a treatment facility.

Slag Plant

Various useful products are recovered from slag; some being produced from slag in a molten form and others after solidification.

Molten blast furnace slag can be quenched with water to produce lightweight expanded aggregate for the manufacture of cinder block.

It can also be spun into mineral wool insulation. Solid air-cooled slag is crushed to various sizes for use as track ballast, highway foundation, and similar structural material.

In plants handling slag, airborne dust normally tends to cake onto conveyor belts or interfere with proper operation of mechanical equipment. Water washing of air is sometimes practiced. Water may be used for washing conveyor belts, thereby creating high suspended solids wastewater.

BOF, open-hearth, and electric furnace slags are very high in iron. Therefore, they are usually broken up and reclaimed for charging to the blast furnace.

Utilities

Because of useful combustible gases produced at coke ovens and blast furnaces, steel mills are able to produce a large percentage of their total power requirements by burning these fuels in boiler houses. In addition to boilers directly fired with these by-product fuels, other boilers can reclaim heat from gases discharged from basic oxygen and open-hearth furnaces. Steam generated by these boilers is used throughout the mill for driving turbines, powering water pumps, presses, and forges, and providing heat wherever it may be required.

In addition to production of power from steam, some by-product gases are used in gas engines to produce electric power or mechanical energy directly for such uses as compressing air for blast furnaces. Other utilities include air compressors, vacuum pumps, and pump stations to supply the enormous quantities of air and water needed.

Water requirements for these utilities in the steel mill are similar to those of other industries. High-quality water must be produced for makeup to steam generators, and these in turn concentrate the water, which is then removed at a relatively high salinity level. Water treatment facilities required for producing this high-quality water generate their own wastes, such as lime sludge from lime softening operations, brine from ion exchange softening operations, and spent acid and caustic from demineralizer regeneration.

Cooling water is used by these utilities for such purposes as condensing turbine exhaust, cooling compressor jackets, cooling bearings on various types of powerhouse auxiliaries, and conveying ashes from coal-fired furnaces.

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CHAPTER 39

The Institutional and Commercial Sectors

Many universities, hospitals, office buildings, hotels, resorts, and shopping centers use water-based heating, ventilation, and air conditioning (HVAC) systems for controlling internal environment. These facilities use hot water systems or steam boilers for heating, and refrigeration systems for air conditioning. While the individual equipment might appear quite different from one application to another, the basic systems for either heating or cooling are quite similar.

The problems encountered in water-based heating and air conditioning systems in buildings and institutions are similar to those in industrial plant systems (corrosion, scale, fouling, and microbial growth), but the impact of these problems on the operation of the facility can be quite different. First, the consequences of improper water treatment may be more critical to a hospital or residential complex, than to a large industrial plant, since human health, comfort, and even survival may be at stake. Second, heating or cooling is often required intermittently or on an instantaneous basis, so the system may be severely stressed physically, from a water treatment perspective.

Heating and cooling systems in modern commercial, institutional, and residential facilities require good water treatment to maintain efficiency and maximize value. Sophisticated chemical treatment and control systems can help provide the needed system control. This chapter will discuss the various types of heating and refrigeration systems found in these applications.

In a typical institutional or commercial facility, the HVAC system is usually one of the largest consumers of electricity. Figure 39.1 shows the relative distribution of the typical utility costs for building operation. Energy for heating, ventilation, and cooling is the largest cost component. Energy needed for building lighting is a distant second.

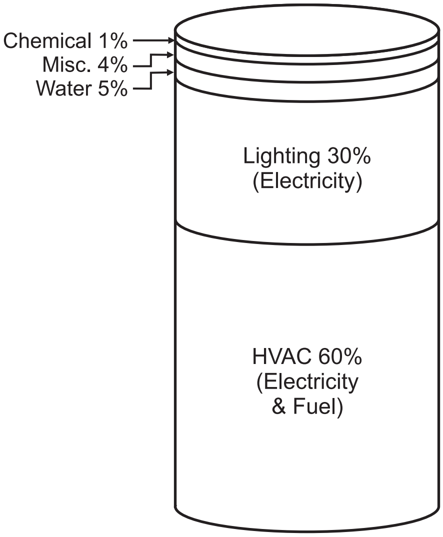


Figure 39.1 Typical utility budget distribution for a commercial building.

Chemical treatment cost variations have an insignificant effect on the overall utility budget. A treatment program designed to help maintain the efficiency of the heating and cooling systems will provide far greater value to a facility than a cheap treatment program. The efficiency of the heating and cooling equipment will become more important as energy demand and fuel costs continue to rise.

Heating Systems

The two basic types of water-based heating systems are steam boilers and hot water "boilers," which are more appropriately called hot water heaters. Steam boilers are usually packaged firetube or watertube design operating below 200 psig (1.4 MPag) (Fig. 39.2). However, in more sophisticated installations, such as an energy supply complex for a large medical center or a large university campus, cogeneration systems with high-pressure [900–1200 psig (6.2–8.3 MPag)] boilers may be used. The high-pressure steam from the boiler drives a turbine to produce electrical energy, and the discharge steam [approximately 100 psig (0.69 MPag)] is used in the heating system. In areas where air conditioning is required in summer, the steam can be used to power an absorption chiller. In this way, energy efficiency is maintained throughout the year.

Most small institutional boilers are usually gas or oil fired, but occasionally, an electrically heated boiler is found. Fuel oils can range from No. 2 to No. 6, including mixtures of several grades.

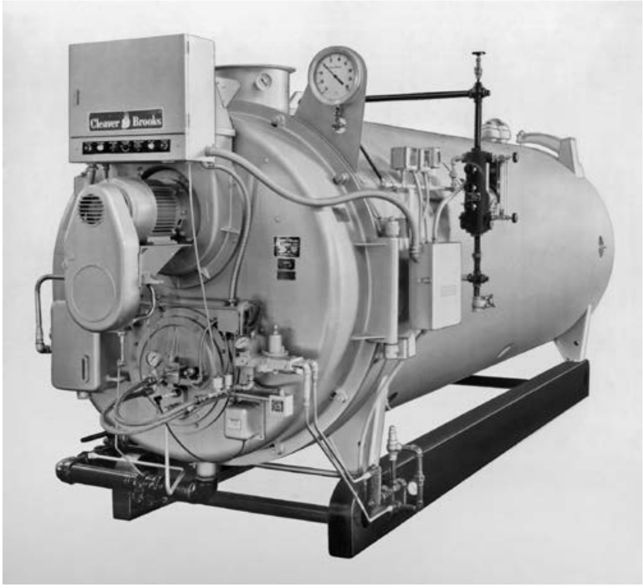


FIGURE 39.2 Typical packaged steam generator with complete fireside and waterside controls. (*Courtesy of Cleaver Brooks, Inc.*)

Many boilers contain burners designed to burn gas or fuel oil, a useful feature in areas where fuel shortages can occur. Coal-fired boilers in commercial buildings and institutions are rare, but can be found in some larger cogeneration systems.

Steam Boilers

In heating applications, the steam generated in these boilers is used in one of two ways. First, steam may be directly circulated throughout the building, where the heat is extracted through radiators or fan-coil units, and the condensate is returned to the boiler to be used as feedwater. In the second method, steam is used indirectly to heat a closed hot water loop that circulates hot water to the fan-coil units throughout the building. The heat exchanger for heating the hot water loop is located relatively close to the boiler, and the condensate returns to the boiler. Steam can also be used for humidification, sterilizing, kitchen, and research purposes.

Boiler Operation and Potential Problems

The boiler operation depends on the boiler design and the quality and pretreatment of the makeup water used to produce the feedwater to the boiler. Refer to Chap. 9 on Boiler Systems for more details on boiler operation. Ideally, low hardness, low oxygen, and low alkalinity water is used. The requirements of the feedwater depend on the size and operating pressure of the boiler. In a low-pressure boiler [<1000 psig (6.9 MPag)], the water may be only softened to reduce the hardness, leaving alkalinity and other dissolved solids in the feedwater. In a high-pressure boiler [>1000 psig (6.9 MPag)], the water may be demineralized or utilize reverse osmosis technology to remove the majority of dissolved solids. Most steam boiler systems use a deaerator to remove dissolved gases from the feedwater before it enters the boiler.

Boilers can experience scale formation, corrosion, and metal oxide deposits, depending on the operating characteristics, feedwater quality, and treatment practices. Any residual hardness in the feedwater can produce scale on the boiler internals. Hardness scales, like calcium and magnesium carbonate, occur due to the decreasing solubility of these minerals as temperature increases. These scales can form in the feedwater system and in low-pressure boilers, where no feedwater pretreatment or poorly maintained softening is used. Silica-based deposits can be found in low-pressure boilers, where the pretreatment system is not designed for removal of silica from the feedwater, or the boiler is operating at excessive cycles of concentration. Scale deposits reduce thermal conductivity of the boiler, reducing thermal efficiency and reliability. As a result, more fuel may be required to produce the same amount of steam, increasing operating costs.

Corrosion can occur in various parts of a boiler system. If dissolved oxygen is not controlled, corrosion can occur from the deaerator to the final condensate system. However, oxygen corrosion is rarely found inside an operating watertube boiler. Oxygen corrosion found in watertube boilers is generally the result of improper lay-up procedures. Oxygen corrosion can be a greater problem in the condensate system.

The iron generated from corrosion in other parts of the system can cause metal oxide deposits in the boiler. Corrosion of the feedwater piping and iron entering with the makeup water contribute to iron deposits. Most of the corrosion products that deposit in the boiler originate in the steam condensate system. These metal oxide deposits can cause under-deposit corrosion and overheating problems in the boiler.

Condensate Systems

The goal of the condensate system is to recover the hot pure water after the steam condenses and return this water to the boiler (see Chap. 13 on Condensate Systems for more detail). The system design depends on the type and size of the heating system. The condensate return system of a university can be complex and is subject to unusual corrosion problems, because of the stress of seasonal changes. Condensate is ultra-pure water and is very aggressive to most metals used in these systems. The main contaminants that can increase corrosion in the condensate system are gases, like carbon dioxide (CO_2) and oxygen (O_2). Carbon dioxide results from the thermal decomposition of alkalinity in the boiler water. The CO_2 dissolves in the condensate and produces carbonic acid (H_2CO_3). This acid decreases the pH of the condensate and increases corrosion of steel and copper alloys.

Dissolved oxygen can enter the system from either the feedwater or ingress of air into the condensate system. Oxygen inleakage can be difficult to control due to the many potential sources, such as condensate tanks, pump seals, and vacuum breakers on steam coils. The result is oxygen pitting in the condensate system, which can be quite severe, as shown in Fig. 39.3.

In HVAC systems, a common source of air inleakage is the vacuum breaker found on heating coils in air handlers. The vacuum breaker allows air to enter the coil to eliminate a potential vacuum inside the coil when the steam flow stops. If the vacuum is not relieved, the coil could collapse. In a large HVAC system, there may be hundreds of fan-coil units, each with a vacuum breaker. Intermittent operation of the entire system can cause inleakage as a vacuum is created during idle conditions. This is particularly true during spring and fall heating seasons, when heat may be required at night but not during the day. A steam heating system under these conditions is subject to oxygen corrosion during the daylight hours, when condensate receivers cool and draw in air.

Boiler Lay-Up

A boiler may not need to be operated continuously, depending on the building and the need for steam. When boiler operation is stopped,

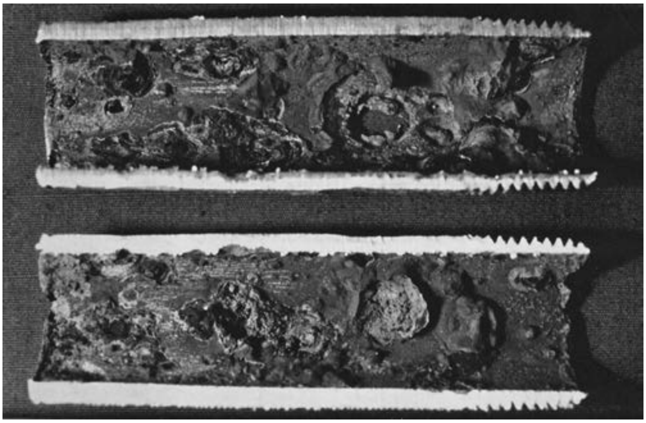


FIGURE 39.3 Severe oxygen corrosion on the internal surface of a condensate line.

air can leak into the boiler as the internal pressure decreases. Oxygen corrosion, which often occurs as pitting corrosion, can occur during out-of-service periods. Oxygen corrosion can be a major contribution to reduced equipment service life. During idle periods, proper lay-up procedures must be followed to minimize corrosion problems and ensure the boiler is ready to start up again when needed. Two different methods for boiler lay-up are wet lay-up and dry lay-up. In wet lay-up, the boiler is left full of water, and this water must be treated to maintain low oxygen content and appropriate pH. In dry lay-up, the boiler is drained of all water and typically maintained dry with either nitrogen or desiccant.

The choice of lay-up method generally depends on the length of time the boiler will be offline. Wet lay-up is most often used for short outages (30 days or less) and when the boiler may need to be started again on short notice. Dry lay-up is generally used for longer outages and is practical only if the boiler can be drained when it is hot.

For specific boiler lay-up methods and procedures, the reader is directed to "Consensus for the Lay-up of Boilers, Turbines, Turbine Condensers, and Auxiliary Equipment" published by the American Society of Mechanical Engineers (ASME).

Boiler and Condensate System Treatment

Water treatment in these steam plants is similar to that used in most industrial boilers. The chemical products should control scale, corrosion, and fouling in the boiler, as well as corrosion in the condensate system (see Chap. 11 for more details on boiler treatment methods). The types of products used are similar to those used in industrial systems; however, treatments may be blended and packaged so as to be convenient and easy to handle, feed, and control. Automated monitoring and control programs can make chemical treatment programs more effective and reliable.

The steam generated in these boilers can have other uses, such as humidification, dishwashing, food preparation, and sterilization in autoclaves (as in hospitals and research laboratories). A careful study must be made of the uses to which the steam is put so that acceptable and safe treatment chemicals can be used. If any part of the steam contacts food, for example, U.S. Food and Drug Administration (FDA) approved treatment chemicals are required.

In extensive condensate systems, where oxygen inleakage may be a common problem, complex feed systems may be required. In addition to a central chemical treatment station in the boiler house, satellite systems are sometimes installed to supply additional steam treatment to correct for seasonal upsets or depletion of the treatment. The quality of the condensate must be under constant surveillance to minimize any negative impact to the boiler. Continuous monitoring and control systems can be a significant benefit in large systems. Ion exchange condensate polishers are commonly installed in the boiler house to remove condensate contaminants, and prevent having to discard large amounts of valuable hot condensate. Monitoring conductivity at significant condensate return junction points helps to locate and isolate the failure promptly. Installation of sample coolers should be utilized to ensure safe sampling habits and maintain sample integrity.

Hot Water Systems

Hot water “boilers” are really misnamed, since they do not boil water and produce no steam. They can heat water to 500°F (260°C), but typically operate at temperatures of 180 to 250°F (82–121°C) in a vessel similar to a steam boiler. The heated water is circulated through the building to various heat exchangers and radiators and back to the boiler. The heat source for these boilers may be natural gas, fuel oil, or electricity. Electric boilers use either enclosed clad-type immersion heaters or resistance heaters, which operate by a flow of current between electrodes in the boiler water. The boiler water is conductive because of its mineral content.

Hot water systems are designed to be closed. Theoretically, there should be no makeup water required, but normally, a small amount is required to replace water lost by leakage of liquid or vapor. In these systems, the primary concern is prevention of corrosion caused by oxygen in the water. In a system with little leakage, the oxygen will be depleted, and corrosion will be minimized at this low oxygen concentration. However, corrosion can be a problem in systems where leakage causes continuous makeup demand. Scale formation, although not usually a major factor, can also occur in hot water boilers. This may be caused by a combination of hard water used to fill the system initially, continuous makeup to replace losses, and the high temperature of the boiler tube surfaces. The gradual accumulation of calcium and alkalinity precipitates calcium carbonate ($CaCO_3$) scale. In addition, foaming can occur, which can cause cavitation corrosion on recirculating pump impellers. Cavitation is loss of metal caused by the impingement of bubbles on the metal at high velocity.

Standard treatment programs for closed systems are the preferred chemical treatment in hot water systems. Such products contain a mixture of corrosion inhibitors to protect steel, aluminum, copper, and admiralty brass, and possibly a scale control agent. This treatment is initially charged at high dosage levels for maximum protection. For those systems containing aluminum, special caution should be applied to maintaining the system pH between 8.0 and 8.5 due to the amphoteric properties associated with that metal. Since hot water systems have little makeup and treatment chemicals are relatively stable, only small additions of treatment are required thereafter to maintain protection.

Cogeneration Systems

Because energy efficiency is increasingly important, many large facilities, especially universities, are installing cogeneration power plants. Systems that generate electrical power and use the excess heat for heating or cooling purposes are called cogeneration or combined heat and power (CHP) systems. The goal of these systems is to improve the energy efficiency of the basic power generation cycle. Production of electricity by the best conventional power plants converts only 40 to 50% of the fuel energy into electricity. The remainder is lost as heat. This heat, in the form of low-pressure steam, can be used to heat buildings, produce hot water for general use, or power an absorption chiller for air conditioning additionally, the steam produce can be utilized to drive steam driven pumps. When used for electrical production, heating in winter, and cooling in summer, these systems can improve the efficiency up to about 80 to 90% of energy in the fuel being converted to useful power.

CHP systems are used in a variety of large building facilities, university campuses, or for district heating systems. Many universities have CHP systems, including the Massachusetts Institute of Technology and the University of California at Berkeley, both of which have 25 MW generation facilities. Denmark has a large number of CHP systems, some of which burn agricultural waste for fuel and the excess heat is used for heating greenhouses.

CHP systems are common in municipal district heating systems in large cities around the world. Some of the largest district heating systems are found in:

- St. Petersburg, Russia
- Prague, Czech Republic
- Warsaw, Poland
- Seoul, South Korea
- New York City, USA
- Stockholm, Sweden

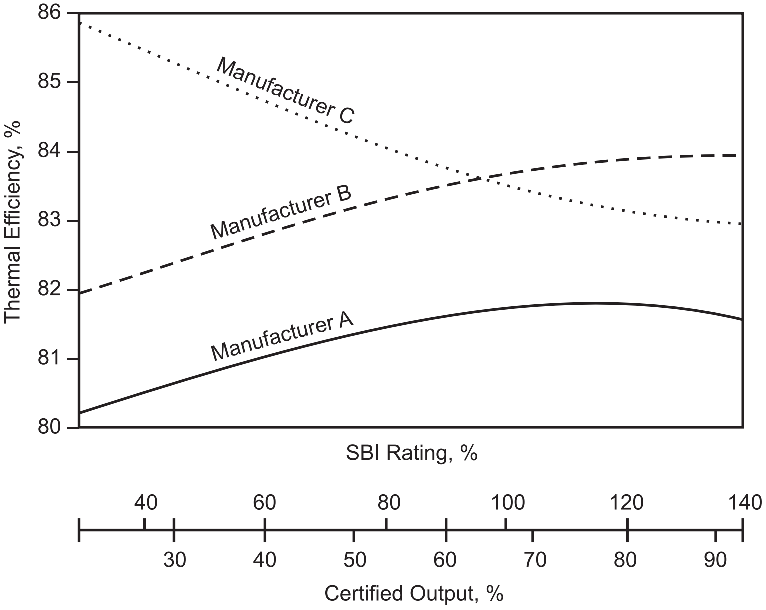
Collection of condensate can be more challenging in these systems because of their size, but it is important due to the purity and energy content of the condensate.

Heating System Efficiency

Energy costs for space heating in U.S. commercial buildings can be 50 to 60% of the total energy costs for HVAC, according to the U.S. Department of Energy (DOE). The combined efficiency of all parts of the steam system must be considered when evaluating these costs. The efficiency of the heating system depends on the boiler type and design, operating characteristics, and the design of the condensate recovery system. Maintaining the efficiency of the boiler and condensate system can have a significant impact on the utility budget of any facility. Improvement in boiler efficiency by only 1% can provide significant energy savings.

The overall efficiency of the boiler is generally considered to be the fuel to steam conversion efficiency, also called the total thermal efficiency. This is calculated based on the total steam produced, divided by the fuel input, and multiplied by 100 to yield a percent value. This efficiency value is usually calculated using units of energy use per time, such as Btu/h (kJ/h). Accurate inputs are needed to give a meaningful result.

Boiler efficiency depends on the boiler design, operating conditions, and steaming rate. The efficiency for a given boiler will change as the steaming rate changes, as shown in Fig. 39.4. The blowdown rate also affects the efficiency of the system. Blowdown is water removed from the boiler to limit the concentration of ions in the boiler water. The amount of blowdown defines the cycles of concentration of the boiler. Generally, blowdown is in the range of 1 to 25% of the feedwater flow. Lower blowdown means higher cycles of concentration. Since blowdown is very hot water, heat recovery can improve



Certified test by manufacturer

Figure 39.4 Typical packaged boiler performance curves illustrate the efficiency change as a function of steam output.

system efficiency. In some systems, the blowdown is discharged to a flash tank, which produces low-pressure steam that can be used for heating. The greatest benefit from flash tanks can be achieved when the low-pressure steam can be used for other heating purposes, or in the deaerator. In addition to flash tanks, a heat exchanger can be used to preheat the makeup water with the unused heat in the blowdown commonly referred to as blow down heat recovery.

Return of condensate is important because of the heat content and purity of this water. Recovered steam condensate reduces the amount, pretreatment, and preheating of boiler feedwater. Heating systems in office buildings and institutions should return at least 80% of the steam as condensate.

Air Conditioning Systems

An air conditioning system is a mechanism designed to move heat from inside the building to the outside. When cooling below ambient temperature is desired, a refrigeration unit is needed. Air conditioners for households and small buildings use air-cooled refrigeration units. Most large buildings, shopping centers, data centers and similar installations use water-cooled air conditioning units, commonly referred to as refrigeration machines or chillers. Chiller systems have three component parts (Fig. 39.5). First, the chiller is in the center, consisting of the condenser, compressor, and evaporator, which produces chilled water. Second, the chilled water is circulated in a closed cooling water system to remove heat from the building. Third, the heat from the building, removed by the chiller, is generally rejected to the atmosphere by an open recirculating cooling water system. Treating and operating these systems is much like other closed and open recirculating cooling water systems. However, chiller systems have some differences from other cooling systems, because of the importance of efficiency in chiller operation.

Servicing cooling systems on chillers requires an understanding of the operation and economics of these systems. Some chilled water systems are very small, with less than 1000 gal (3.8 m^3) volume. Others, especially those on large university campuses and thermal energy storage (TES) systems, can contain more than 7 million gal (26 500 m^3). While large chilled water systems are complex, the refrigeration equipment is the same as that for a small chilled water system, and the operation and control are quite similar.

Chillers generally fall into two categories—vapor-compression and steam-absorption units. In these chiller systems, a gaseous refrigerant is used within the chiller. There are two types of vapor-compression units—reciprocating compression units and centrifugal refrigeration units, which have similar cycles.

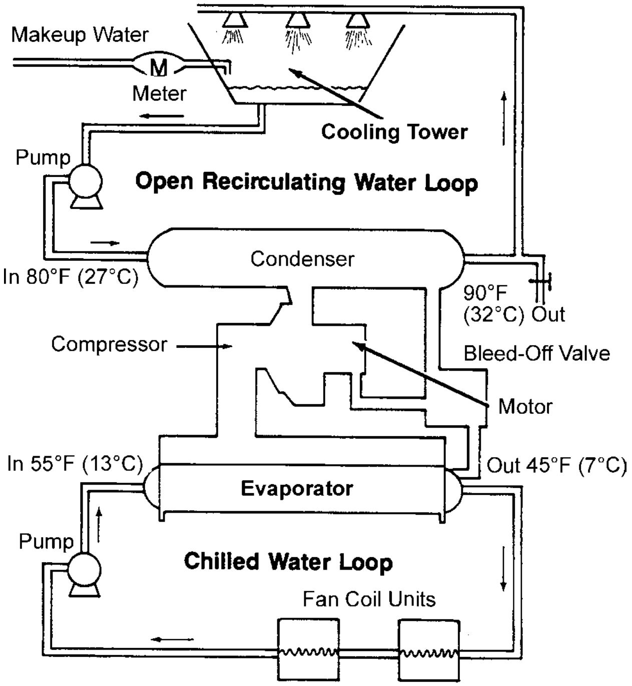


Figure 39.5 Complete air conditioning system schematic, showing the open cooling water system connected to the condenser and closed cooling water loop connected to the evaporator.

Vapor-Compression Units

Reciprocating compressor units are systems in which the refrigerant is compressed in a reciprocating compressor, which is driven by an electric motor. A complete system containing the compressor, condenser, and evaporator combined into one unit is shown in Fig. 39.6.

Centrifugal refrigeration units compress the refrigerant by a centrifugal compressor driven by an electric motor, a steam turbine, a gas engine, or a gas turbine. Packaged units that contain the compressor, condenser, and evaporator are available (Fig. 39.7).

The refrigeration cycle in a vapor-compression chiller is illustrated in Fig. 39.8. The description of the refrigerant cycle will start in the condenser, in the upper right of Fig. 39.8. In both reciprocating and centrifugal vapor-compression units, the hot compressed refrigerant vapor first passes through a water-cooled condenser. The condenser is usually a shell-and-tube heat exchanger, where the refrigerant is cooled and condensed into a liquid. From there, the liquid is sometimes stored in a reservoir. The flow of liquid refrigerant into the evaporator is controlled by a temperature-controlled valve, also called the

Figure 39.6 Reciprocating chiller in a packaged unit. (*Courtesy of the Trane Company*.)

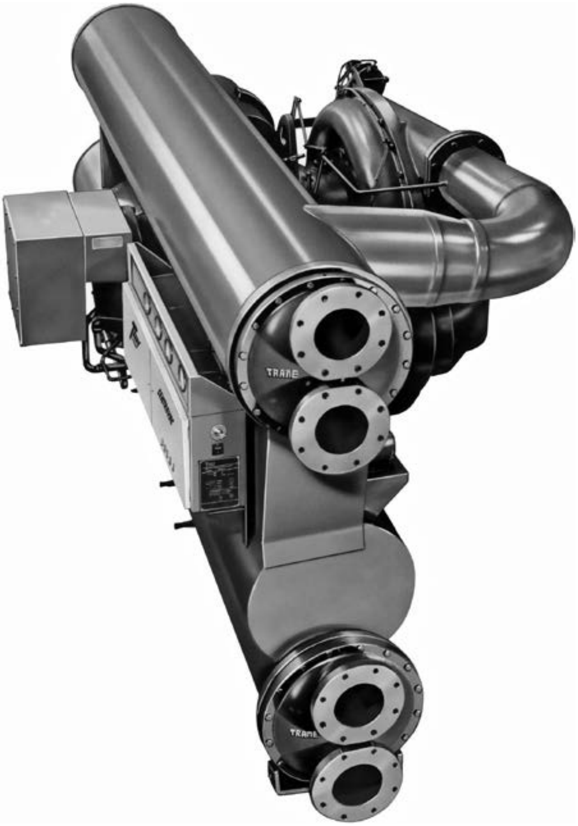


Figure 39.7 Packaged centrifugal refrigeration unit. (*Courtesy of the Trane Company*.)

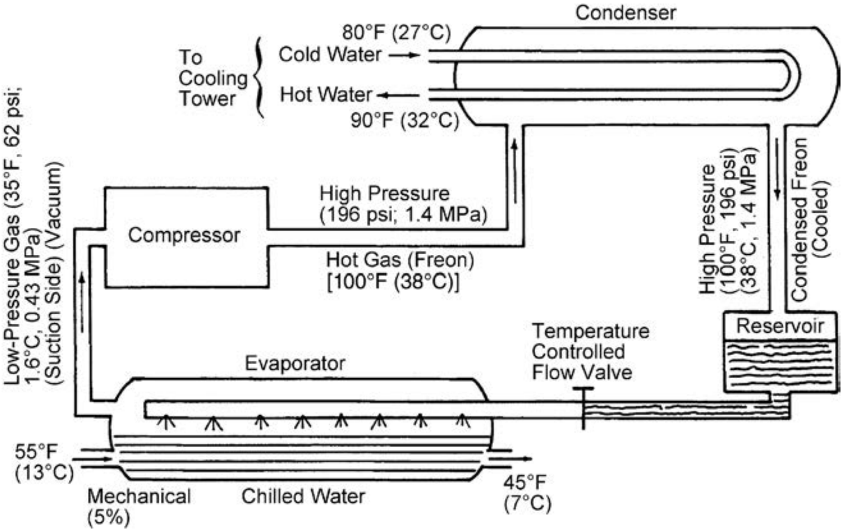


FIGURE 39.8 Typical vapor-compression chiller system schematic, illustrating the compression and expansion cycle of the refrigerant.

expansion valve. When the liquid refrigerant enters the evaporator, the liquid rapidly expands under reduced pressure into a cool vapor, which absorbs heat from the chilled water loop on the other side of the evaporator tubes. The chilled water is generally cooled from about 55°F (13°C) to about 45°F (7°C) in the evaporator. The air being cooled in the building warms this chilled water back to 55°F (13°C) before return to the chiller. The refrigerant vapor is then drawn out of the evaporator by the suction of the compressor, where the vapor is recompressed, repeating the cycle. The compressor and the expansion valve separate the high-pressure and low-pressure sides of the refrigerant cycle.

Typical open cooling tower water is used to cool the refrigerant in the condenser. In many cases, evaporative condenser towers are used for this purpose. In evaporative condensers, the condenser coils are placed directly in the cooling tower, and the open loop cooling water passes over the condenser coils as the water falls through the tower (see Chap. 14 on Cooling System Dynamics for more information on evaporative condensers).

Steam-Absorption Units

Regulations governing the use of refrigerants, and the increasing cost of electricity, have prompted many utility managers to consider alternatives to vapor-compression chillers. Steam-absorption refrigeration can be more environmentally friendly and economically

Figure 39.9 A steam-absorption refrigeration system, illustrating the four different chambers required for the complete cycle. (*Courtesy of the Trane Company*.)

appealing, even though it is one of the oldest technologies available. This is because it uses water as the refrigerant. In addition to the environmental issue, absorbers can allow a customer to utilize steam boilers more efficiently.

An absorption chiller may be constructed in one, two, or more shells or sections depending on the manufacturer and the application (Fig. 39.9). The steam-absorption unit cycle is more complicated than vapor-compression unit operation. Steam-absorption units use water as the refrigerant, a lithium bromide solution to create a vacuum by absorbing the water, and steam as a heat source to evaporate the water from the dilute lithium bromide solution. Absorption units use condensers cooled by water from a cooling tower and evaporators to provide chilled water for air conditioning. From the water treatment point of view, the operating principles of the open recirculating and closed chilled water systems are the same in all chillers.

The absorption cycle (Fig. 39.10) consists of the following major components:

- Evaporator section, where the refrigerant (water) is sprayed over the chilled water tubes. The refrigerant picks up heat from the chilled water coils and flashes to vapor. The evaporation of the refrigerant cools the chilled water, which is contained in a closed cooling system. The evaporator is maintained at a vacuum, which causes the refrigerant to evaporate at a much lower temperature than at atmospheric pressure.

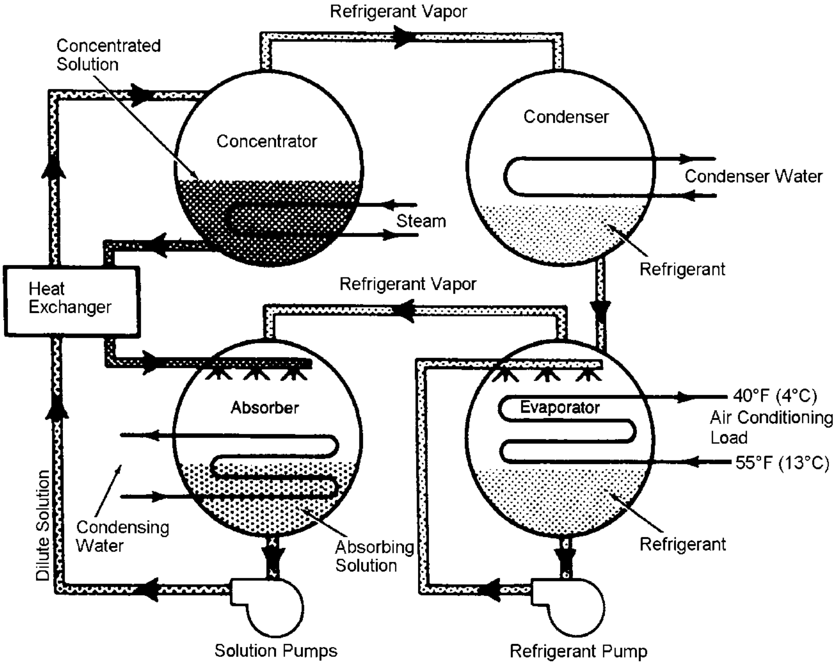


Figure 39.10 Flow diagram for the steam-absorption refrigeration cycle.

This part of the process is essentially the same as that of an evaporator in a vapor-compression chiller.

- Absorber section, where the evaporated water vapor (refrigerant) is absorbed into a concentrated lithium bromide solution. The hot concentrated lithium bromide solution is sprayed into the absorber vessel. The water vapor coming from the evaporator is absorbed by the lithium bromide. The heat of absorption is removed by cooling tower water circulated through this section. Absorption of the water vapor produces the vacuum drawn on the evaporator. This vacuum is maintained by controlling the temperature and concentration of the lithium bromide solution.
- Concentrator section, where heat is added by steam or hot water to boil off the refrigerant (water) from the absorbent to reconcentrate the lithium bromide solution. The steam demand is controlled by the temperature of the chilled water. When more cooling is needed, more steam is required.
- Condenser section, where the water vapor (refrigerant vapor) produced in the concentrator is condensed and cooled by condenser water (cooling tower water) circulated through

this exchanger. The cooling water recirculation rate in an absorber condenser is usually higher than in a vapor-compression unit, and the cooling tower range or delta T (ΔT) is usually higher too. Higher skin temperature results, increasing the risk of scaling and microbial fouling on the cooling water side.

- Refrigerant pump, which pumps the refrigerant over the tube bundle in the evaporator section.
- Solution pumps, which pump the lithium bromide solution to the concentrator and to the spray header in the absorber.
- Heat exchanger, where the dilute lithium bromide solution being pumped to the concentrator from the absorber is heated by the hot concentrated lithium bromide solution, which is returned to the absorber.
- Heat recovery exchanger (not shown), may be used in some systems. This exchanger recovers heat from the refrigerant vapor leaving the concentrator, passing the heat to a closed hot water heating loop.
- Purge unit (not shown), which is used to remove noncondensable gases from the machine and to maintain a low pressure in the evaporator.

What is a Ton?

The cooling capacity of refrigeration units is often indicated in tons of refrigeration. A ton of refrigeration represents the heat energy absorbed when one ton [2000 lb (907.2 kg)] of ice melts during a 24-hour period. The ice is assumed solid at 32°F (0°C) initially and becomes water without changing temperature. The energy absorbed by the ice is the latent heat of fusion (melting) times the total weight (mass).

Refrigeration units can be rated in Btu/h, kcal/h, kJ/h, or kW instead of tons. The energy equivalent of one ton of refrigeration is:

- One ton of refrigeration = (2000 lb)(144 Btu/lb)/24 h = 12 000 Btu/h
- One ton of refrigeration = (907.2 kg)(80 kcal/kg)/24 h = 3024 kcal/h
- One ton of refrigeration = (907.2 kg)(334.7 kJ/kg)/24 h = 12 652 kJ/h
- One ton of refrigeration = 3.5145 kW

Unique Chiller Design and Operating Characteristics

New equipment designs and opportunities for more efficient operation can provide significant energy and cost savings. An example of new design includes chillers with enhanced tubes. Operating practices to improve efficiency include free cooling. A thermal storage system involves both design and different operating practices to obtain greater efficiency. These designs and operating practices can lead to unique or greater problems than with standard chiller designs and operation.

Enhanced or Rifled Tubes

Increasing energy costs and use of newer refrigerants are driving the move to high-efficiency chillers. Enhanced tubes are one way to make chillers more efficient. These tubes are usually rifled internally (typically the water side of the tubes), although the tubes can be rifled or finned on the external tube surface (Fig. 39.11). The grooves increase surface area and create more turbulent water flow, making heat exchange more efficient. Enhanced tubes require good water flow and effective water treatment programs, because deposition and fouling can occur more easily in the grooves of the tubes when low flow or inadequate water treatment occur.

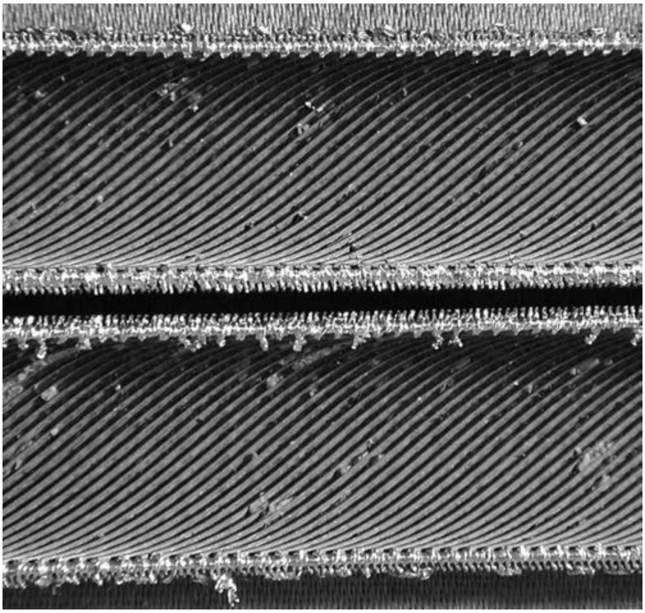


Figure 39.11 Rifled condenser tube split longitudinally. The deposits are the result of localized corrosion in the grooves.

Corrosion in copper tubes used in HVAC systems is generally uniform oxidation, pitting, stress corrosion cracking, or corrosion fatigue (see Chap. 16 on Cooling System Corrosion for more details on these forms of corrosion). Rifled chiller tubes can have additional failure modes, including erosion corrosion from flow variations over the groove, under-deposit corrosion from fouling of the rifled groove, and microbiologically influenced corrosion (MIC). A unique type of pitting that looks like an ant's nest when viewed in cross section is also seen in prematurely failed rifled tubes. This is sometimes called formicary corrosion. These pits can be branched, and the pinholes penetrating the copper walls are generally difficult to detect by the naked eye.

Several factors can influence failure of enhanced tubes, even before the tubes are installed. Lubricating oils used during tube manufacture can decompose into products that include carboxylic acids, acetates, and chlorides under the proper conditions of moisture, oxygen, and warmth. The presence of such corrosive chemicals initiates ant's nest corrosion, which can propagate before and after tube installation. Copper tubes may be stored under conditions of high humidity, which is known to worsen localized corrosion. In general, uniform copper dissolution occurs under total immersion in the water. However, in the presence of humidity, a thin layer of water molecules can occur in localized areas on a copper surface. This can increase the localized corrosion rate.

After tube installation, problems including deposition, low water flow, or poor treatment control can cause failure during normal operation. Corrosive substances can be present at the time of tube installation or develop over time by possible leaks (e.g., refrigerant). As mentioned above, there may be residual organics either from incomplete tube cleaning or from trace amounts of detergents and solvents. Suspended solids, scale, corrosion product, and microbial deposits will form more easily in the grooves of rifled tubes. Any of these deposits can cause under-deposit corrosion. Microbial deposits can also cause MIC. Prevention of these problems is more critical with enhanced tubes.

Intermittent operation of a chiller system can cause low or no cooling water flow. HVAC systems often do not operate on a continuous basis, and operators will shut chillers down periodically. This results in stagnant water inside the tubes, where suspended solids can settle and deposit easily on the tube surface. The situation is worsened when these deposits remain in the grooves of rifled tubes and eventually cause under-deposit corrosion.

Ineffective water treatment and poor system control can cause problems. Low dispersant levels allow mineral scale particles or suspended solids (silt and dirt) to deposit in the grooves of these copper tubes and initiate under-deposit corrosion. Low levels of copper corrosion inhibitor can lead to poor corrosion control, which can contribute to tube failures. In addition, poor microbial and system flow control will cause microbial colonies to develop and flourish. MIC will then become a factor in tube corrosion and failure.

Preventing problems in enhanced tubes requires many of the same practices that are required for smooth exchanger tubes. However, maintaining systems with enhanced tubes may require extra steps or require more careful monitoring. The practices for systems with enhanced tubes can benefit any system. The appropriate treatment program should be used in systems for both the condenser and evaporator cooling water systems. A standard closed system treatment program should be used to provide the necessary general corrosion, deposit, and microbial control. Maintaining the appropriate copper corrosion inhibitor concentration in the system is important.

For the open system serving the condenser, treatment can be more challenging. Any new system should be cleaned and passivated before starting a water treatment program. A treatment program should be selected based on the water chemistry, system characteristics, and operating temperatures to maintain control of corrosion, deposition, and microbial growth. Prevention of fouling by scale, corrosion, suspended solids, and microbial growth is essential.

Free Cooling—Opportunities and Challenges

Free cooling assumes that outdoor air temperature is low enough to provide cooling without running the chillers. This practice is useful when the outside temperature is below 45 to 48°F (7.2–8.9°C) and heating is not yet required in the building. In some parts of the world, free cooling is an option for 30 to 40% of the year.

In older free cooling systems, tower water was mixed with the chilled water system (direct injection) to provide free cooling. Both the chilled water system and the open cooling tower system will suffer when these waters are mixed. Examples of these problems include:

- Dirty tower water enters the relatively clean chilled water system.
- Microbial loading on the chilled water loop increases.
- Incompatible treatment chemistry mixes in the open and closed cooling water loops.
- Expensive closed loop treatment chemicals are lost.

As a result, costs for maintenance, downtime, water, chemicals, and energy can be higher when mixing open and closed system water.

Today, mixing the tower water with the chilled water is discouraged, because of the many operational problems that are created.

A heat exchanger can be used to isolate the two water systems. Improvements in plate-and-frame heat exchanger performance have made modern free cooling a very desirable option. New plate-and-frame heat exchangers have design approach temperatures of less than 2°F (1.1°C). This means that when outdoor temperature is 48°F (8.9°C), chilled water temperature can be lowered to 50°F (10°C). The chiller operation is not necessary if outdoor temperature is at or below 48°F (8.9°C). The only energy cost is the energy needed to run the recirculating pump.

Lay-Up

Most chillers do not run continuously, and much of the water-side damage occurs during the offline (idle) periods. Allowing chillers to sit idle containing stagnant water for extended periods is a recipe for failure. Good offline practices are necessary to minimize corrosion and deposition. Maintaining flow with treated system water is the best approach. Dry lay-up is effective, but is inconvenient and does not allow rapid start-up of the idle machine.

Steam-absorption chillers have one unique characteristic concerning lay-up or idle periods. Since absorption chillers use steam as the energy source, condensate corrosion is a concern. The temptation is to valve off the steam side when the chiller is offline. However, steam valves often leak, and isolating the equipment can lead to condensate accumulation in the concentrator. Carbon dioxide can accumulate on the steam side, since CO_2 is a common contaminant in many steam sources. The combination of condensate and CO_2 can lead to highly corrosive conditions in localized areas. The best method to prevent steam-side corrosion during idle periods is to allow a small amount of steam to flow through the idle chiller. If desired, the steam discharge can be captured and reused, but the heat recovery system must not allow condensate to form in the chiller. All condensation must occur outside the chiller to avoid chiller corrosion.

Cleaning

Most closed loops will require cleaning eventually, unless sidestream filtration is used to remove debris. Sidestream filtration is often recommended in all closed loops to avoid the need for online or offline cleaning. Filtration equipment should be sized based on the ability to filter anywhere from 2 to 20% (as economics dictate) of the system volume per hour down to 0.25 microns in porosity. Online cleaning rarely removes more than 50% of the debris accumulated during operation of the system. Offline cleaning can remove most of the debris but is more expensive and time consuming. With offline cleaning, the system is not available for cooling during the cleaning, which can be impractical, impossible, or extremely expensive for the plant.

Cooling System Treatment

In any chiller system, careful attention must be paid to the treatment of both the open recirculating water system and closed chilled water system, whether the exchangers have enhanced tubes or normal, smooth tubes. This is necessary for water-cooled air conditioning systems to operate at design efficiency. A total treatment program for both the open cooling water system and closed loop chilled water system is necessary to minimize corrosion, deposition, and microbial growth.

Closed Chilled Water Systems

The primary goals in treating these systems are to prevent metal corrosion and fouling and to control microorganisms. Closed chilled water systems are generally less susceptible to scale formation, since no evaporation should occur in a properly operating system and water temperatures are low. However, leaks can increase the potential for scale formation from loss of treatment and continuous influx of scale forming ions. Standard closed cooling system treatment programs can prevent these problems and maintain system efficiency.

Microbial growth can be a problem in chilled water systems. Specific problems can be caused by denitrifying, iron and sulfate reducing bacteria (see Chap. 17 on Cooling Water Biology). These microbes cause corrosion of the system metal, which can become severe. Proper control is maintained by periodic analysis of the water and by the application of biocides, when necessary. Biodispersants and biodetergents might also be appropriate.

Open Recirculating Systems

Programs for cooling tower systems must emphasize cleanliness of the chiller condenser, good copper and mild steel corrosion control, and proper microbial control. The chiller condensers have copper-based tubes, in most cases. The copper corrosion and microbial control must be balanced, since oxidizing biocides can influence copper corrosion and impact some copper corrosion inhibitors.

Cooling System Efficiency

Figure 39.12 shows a typical distribution for the energy used by refrigeration systems to provide the desired cooling. Note that the chiller consumes about half of the total cooling energy, while the water circulating pumps (for both evaporator and condenser) consume most of the remainder.

Table 39.1 shows typical costs for refrigeration systems used in different applications. The lower cost for universities is due to the reduced demand in the summer when most students are not in attendance. An office building, like the Petronas Twin Towers in Kuala Lumpur, Malaysia, has 4.25 million ft^2 (395 000 m^2) of floor space.

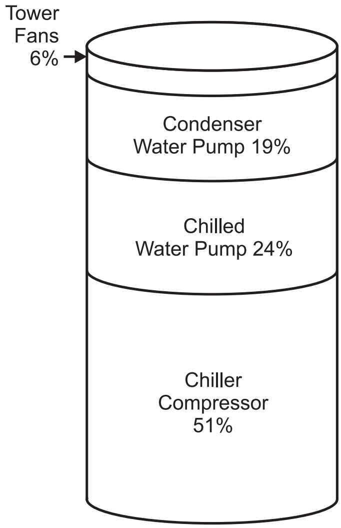


FIGURE 39.12 Typical chiller power consumption distribution.

If the annual cooling operating cost were $2.00/ft^2 ($21.53/m^2), the total cooling bill would be about $8.5 million/yr. Air conditioning is probably required all year in Kuala Lumpur because of the average temperature range of 72 to 90°F (22–32°C). While large facilities like this have a significant stake in maintaining peak performance to minimize cooling energy cost, even small facilities can benefit from good chiller maintenance and operation.

Unfortunately, chillers are often operated inefficiently or maintained poorly, resulting in higher energy costs, lower system performance and reliability, and shortened equipment life. The most common factors that contribute to reduced chiller efficiency include:

- Poor operating practices
- Ignored or deferred maintenance
- Poor cooling tower maintenance
- Oversized equipment
- Ignored energy saving features

Type of Building	$/Gross ft^2	$/Gross m^2
College/University	0.5–0.7	5.4–7.5
Office building	1–3	11–32
Hospital	1.25–3	13–32

TABLE 39.1 Typical Annual Operating Costs for Chiller Systems

Each of these factors affects chiller efficiency significantly, but all can be easily controlled or eliminated by proper operation and maintenance.

Thermal Energy Storage Systems

In some parts of the world, electric utilities offer lower electrical costs during off-peak hours, typically between 9:00 P.M. and 10:00 A.M. each day. One way to take advantage of lower off-peak electrical rates for comfort cooling is to produce and store chilled water or ice during the cheaper off-peak hours. During the day when the cost of electricity is higher, cooling is derived from the stored water or ice in the thermal storage tanks. TES cooling does not reduce energy usage, but the cost of providing cooling can be significantly reduced.

The two most common thermal storage designs are chilled water and ice storage. Chilled water TES systems require larger tanks than ice storage systems for equal cooling capacity. Chilled water at 40°F (4.4°C) can provide 20 Btu/lb (46.5 kJ/kg) of cooling, assuming it warms to 60°F (15.6°C) when cooling the building air. On the other hand, ice stores about 144 Btu/lb (334.7 kJ/kg) of cooling power, because of the latent heat of fusion at the freezing point. This makes ice storage more attractive from a system volume size. TES systems typically range from 10 000 to 4 million gallons (38–15 100 m^3) in capacity. Systems as large as 7 million gallons (26 500 m^3) have been used.

TES systems can be categorized as full-load or partial-load. The objective of full-load thermal storage is to shift the entire refrigeration load out of the period of peak electrical cost. The chiller must be sized to handle the entire capacity of the cooling load. The load profile in Fig. 39.13 illustrates full-load thermal storage, which is best utilized when cooling loads are short in duration, especially if they are high. In the partial-load leveling method, the chiller runs continuously, producing cooling capacity in the TES system at night and cooling the building directly during the day with help from the stored cooling. Figure 39.14 shows the load profile of a typical partial-load system. The chiller capacity can be smaller, because it does not need to handle the entire cooling load.

There are some important differences in the chilled water loops between on-demand and TES systems, from a water treatment perspective. The main difference is the storage tank in the TES system, which is not needed in on-demand systems. Therefore, TES systems are generally much larger. The on-demand chilled water system is typically completely closed and therefore a low oxygen environment. In most cases, the TES system storage tanks are open directly to the atmosphere, so the water can be constantly aerated. In-ground multiple-tank TES systems may be located in parking garages or

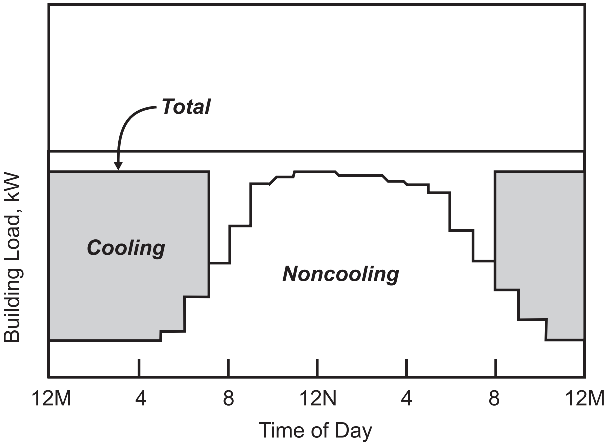


FIGURE 39.13 Full-load thermal storage runs the chillers only during off-peak hours for low electric rates.

other parts of a facility that allow contamination from dirt, rainwater, and other sources. Low flow or stagnant areas may exist in the tanks, where deposits can build up and create areas for microbial growth. Because of their open design, treatment options for TES systems must shift away from traditional closed loop inhibitors like nitrite, mainly due to degradation by microorganisms, which easily contaminate these systems.

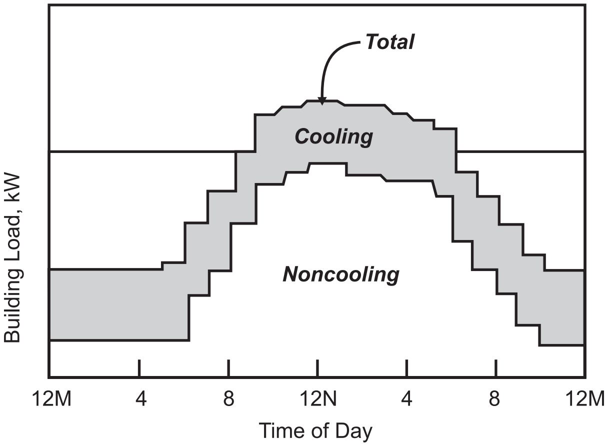


FIGURE 39.14 Partial-load thermal storage runs the chillers during off-peak hours to produce stored chilled water or ice to help minimize the chiller capacity needed during peak electric rates.

Thermal Energy Storage System Problems

TES systems may experience a variety of operational problems due to their unique design. A multitude of factors can result in operational problems:

- Poor system design can cause problems with microbial contamination and sludge buildup in large single-tank systems, if the distribution headers are not designed properly. Deposits can occur in areas of the tank that do not have sufficient water velocity.
- Poor start-up (cleaning and passivation) can cause ongoing problems. Sometimes, only lines and equipment are cleaned and pretreated to remove debris, dirt, and mill scale. However, the storage tank must also be cleaned to allow the corrosion inhibitors to work properly and eliminate sites for deposition, microbial growth, and under-deposit corrosion.
- If water treatment is neglected, active corrosion, large amounts of iron in the water, and microbial growth can occur. These problems can foul the system and reduce energy efficiency.
- Intermittent operation can cause stagnant conditions for extended periods. Corrosion inhibitors can be locally depleted, leading to corrosion and the development of corrosion-based deposits. The lack of flow can affect the distribution of treatment programs throughout the system.
- Inadequate mechanical removal of solids due to the lack of filters can cause sludge buildup in the tanks. Microbial growth in this sludge can contaminate the entire system.
- Lack of designed blowdown or replacement of water can lead to depletion of inhibitors and increased concentration of dissolved solids in the system.
- Open storage tanks can lead to contamination by a variety of materials, including dirt and microbial organisms.

TES offers the opportunity to reduce the cost of energy used for cooling. However, it increases the complexity of the system and its operation.

Thermal Energy Storage Treatment Programs

There is a variety of treatment programs available for TES systems. Control strategies from typical chemical treatment programs, to nitrogen blanketing and oxygen scavenger technology have been proposed. However, the more elaborate the program, the more difficult it is to control and maintain. Corrosion inhibitor treatments should be nondepositing in nature. Dispersant polymers should be included at times (dependent on iron removal ability from on-site side stream filtration) for dispersion of suspended material and iron. Economics of the biocide treatment program often restrict or minimize biocide use in TES systems. The use of nonoxidizers requires slug dosing of the material to achieve a sufficient biocide concentration to kill the bacteria. Typically, low-level feed of nonoxidizing biocides is ineffective for microbial control in TES systems and over use should be discouraged due to the potential for increased COD and TOC buildup from the bio-degradable nature of the products. Oxidizing biocides are not often used, because of the potential for corrosion from buildup of halogen and halides. However, the use of chlorine dioxide as alternate to the more commonly used oxidizing biocides (chlorine, bromine, and hydrogen peroxide) has shown to be effectively in reducing both planktonic and sessile micro-biological activity due to its persistent and elevated oxidative capacity without the related end product issues.

Data Centers

Data centers vary widely in size and design. In the past, computer servers would commonly reside in commercial multi use buildings and HVAC systems would closely resemble that of other commercial and institutional buildings. Past data centers would be a designated space within a building, sometimes as small as a closet or a few floors of a high-rise building.

With the emergence of the public cloud, social networks, mobile phones, and the Internet of things, computer server volume and density have continued to increase the amount of heat generated by the computing load. As densities have increased, so have the numbers and sizes of stand-alone data centers.

The evolvement of the data center industry has changed its cooling system landscape. Today, it is quite common for data center HVAC systems to be built for the single purpose of cooling computer servers and to be optimized for this single purpose. It is also common for servers owned by different tenants to be co-located in buildings occupied only by computer servers, requiring optimized cooling schemes to ensure reliability and efficiency.

Data center cooling systems can be tailored to the local daily outdoor ambient temperatures and humidity, and the cooling strategy aligned to the heat load. Most recently, there has been the emergence of mega data center campuses that contain thousands of servers and multiple cooling strategies at a single site based on the type of heat load being generated.

Water treatment in data centers has become increasingly complex. Design and operating practices can lead to unique water problems specific to a single system within the data center. Typically scale, corrosion, fouling, and microbiological growth are the greatest concern in data centers. These problems are solved with the same principals of water treatment that are utilized in other commercial and industrial HVAC systems. Also, because energy and water usage for cooling takes a significant part of data centers' utility bill, as the data centers grow bigger and bigger, treating water properly and efficiently has become more and more important for the data centers owners.

Data center cooling systems vary widely and are typically customized to the local prevailing climactic conditions. Broadly, the cooling approaches fall under air side economizer cooling strategies and water side economizer cooling strategies. These systems may be standalone approaches or combinations of several different cooling strategies depending on the individual data center needs. A typical evaporative approach involves running water over media with a crossflow of air (see Fig. 39.15).

Air side economizer cooling typically takes the form of one of the following cooling configurations:

- Direct outside air system with direct evaporative cooling (DEC)
- Recirculating (closed) air system with indirect evaporative cooling (IEC)
- Recirculating (closed) direct outside air system, 2 stage indirect-direct evaporative cooling (IDEC)
- Indirect air to air heat exchange with direct evaporative cooling in secondary air (IOA + EC)

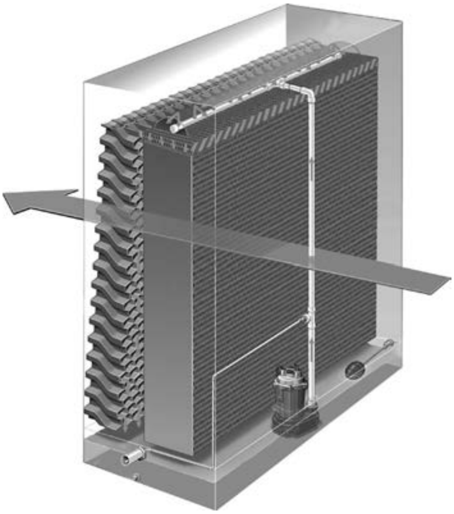


Figure 39.15 Typical data center direct air cooling utilizing evaporative media. (*Courtesy of Munters*.)

- Mechanical cooling
  - Air cooled chiller coupled to chilled water coil in air handling unit (AHU)
  - Direct expansion packaged in AHU or separate direct exchange coil and remote condenser
- Cooling configuration options
  - Interior AHU—direct outside air with direct evaporative cooling
  - Exterior AHU—indirect outside air and indirect evaporative cooling

Water side economizer cooling typically takes the form of one of the following cooling configurations:

- Direct (open) evaporative cooling tower with flat plate (OCT + FP) heat exchange
- Indirect (closed) cooling tower with spray (CCT + spray)
- Mechanical cooling
  - Water cooled chiller (WCC) coupled with chilled water coil in AHU. Typically seen with OCT + FP
  - Air cooled chiller (ACC) coupled with chilled water coil in AHU. Typically seen with CCT + Spray
- Cooling configuration options
  - Computer room air handling unit (CRAH) is perimeter air delivery with chilled water coils
  - In-row unit has the cooling system in close proximity to the server rack with the cold air delivered via module fans and a cooling water coil
  - Rear door heat exchange (RDHx) is a passive form of cooling that combines the cooling coil sans fan within the server rack structure
  - Overhead coil heat exchange (OCHx) is a passive form of cooling that combines the cooling coil sans fan within the server rack structure.

CHAPTER 40

The Food and Beverage Industry

Due to its intimate connection with public health, the food industry has a long history of surveillance of its activities by local, state, and federal agencies. The United States Congress passed the original Food and Drug Act in 1906. With subsequent legislation, that act controls the chemicals that are directly added to food such as salt, seasonings, and preservatives but also such chemicals as sizing in food wrap that may indirectly become food additives by contacting food.

In addition to the close control by the U.S. Food and Drug Administration (FDA), additional surveillance is imposed on meat and poultry processing plants through the U.S. Department of Agriculture (USDA). Chemicals cannot be brought into a meat or poultry processing plant unless approved by the USDA for its intended use, such as equipment cleaning or water treatment. Because of this close regulation, the choices of chemicals used in water and wastewater treatment, may be more limited in the food industry than in other major water-consuming industries.

One of the major long-term trends affecting the food and beverage industry is sustainable development. Sustainable development in the industry can generally be defined as corporate and individual plant performance initiatives with goals to reduce, conserve, reuse, or recycle those resources, which will reduce the corporation's or plant's environmental "footprint." The aim is toward a goal where all the resources, whether they are natural, monetary, or human, are utilized to create, in essence, a zero-use system. Every resource would be fully replenished with a positive impact on individuals, communities, and the environment in which food-processing companies operate.

Sustainable development has three major components: social, environmental, and economic. The industry continues to focus on economic performance and improvement, but with vastly higher awareness and expectation for the total impact of its actions. This trend does not look to abate, and Nalco continues to develop and implement innovative, differentiated solutions that are financially, technically, and environmentally sustainable to contribute to industry and individual location improvements.

Although there are wide variations in the process steps in each of these industry segments, there are a number of common unit operations. The distribution of water in the plant can be put into three categories: process water, cooling water, and boiler makeup water. The percentage distribution varies considerably from a high of about 60% used for processing in the meat and poultry industry, to a low of only 15% in the sugar industry. However, 65 to 75% of the water used in the sugar and ethanol industries is for cooling purposes, with only 25% being used in the meat and poultry industry. Most food processing plants generate steam for cooking or processing, and water used for boiler makeup ranges from about 6% of the total usage in fruit and vegetable processing to about 15% in the fats and oils segment.

Process water uses include washing of raw product and process equipment, transporting product from one process area to another, and as part of the finished product. Cooling water may be used in refrigeration equipment, to condense steam from evaporators or turbines, or to cool process equipment such as compressors, process vessels, engine jackets, or sterilizer equipment.

Steam may be generated for cooking, sterilizing, heating evaporators, cleaning and sanitizing or comfort heating. In some industries, enough steam is required to justify installation of a turbine to extract power from the steam before it is sent to process (cogeneration). If the steam can come into direct contact with food, there are limits not only on what chemicals may be used for both steam and boiler water treatment, but also on their maximum concentrations.

Knowing the processing operations in a food plant is helpful to understanding water use; water may be used sequentially for several purposes. For example, the sugar industry has a very high requirement for condenser cooling water because of the evaporation and concentration of syrups. This cooling water is used for washing cane brought in from the fields before it is discharged, and it is categorized as cooling water rather than process water.

Because the problems of cooling water and boiler water treatment in the food industry are similar to other industries, this chapter will deal specifically with a regulatory review and process water, with some consideration of its contamination, control of foam generated during processing, and final treatment for disposal.

Regulatory Review

Since the beginning of time, people have been concerned with the quality and safety of food and medicine. King John of England put the first English food law into place back in 1202. His law prohibited the adulteration of bread with ground peas or beans. Over the centuries, the food industry has seen an increase in regulation on the local, state, provincial, and federal levels around the world, to ensure that products put on the market are safe, wholesome, and sanitary.

In 1906, the United States Congress put in place the original Food and Drug Act. This act has been amended over the years to increase its scope and depth, but the fundamental objective of this act, to ensure public safety and inform the public properly about products in the marketplace, remains constant. Under this act, manufacturers have a legal obligation to ensure products they market are safe to consume or use by the consumer. In addition, manufacturers have a legal obligation to ensure their products are promoted accurately and honestly based on scientific facts.

From a water treatment perspective, the FDA regulates the safety of all food products, except for meat, poultry, and egg processing. The FDA also regulates the safety of veterinary products, such as livestock feed and pet foods. In the industries where these products are produced, water treatment products are considered a food additive by FDA definition. The definition of food additive is any substance where the intended use results, directly or indirectly, in its becoming a component or otherwise affecting the characteristics of food. Livestock feed is controlled under this regulatory standard, because products used in livestock feed eventually end up in the human food chain.

Up until 1998, the USDA maintained the responsibility to approve products used in meat, poultry, egg, and processed meat product facilities. Registration of products with the National Sanitation Foundation (NSF) has now replaced the USDA approval.

Although many countries follow the USDA and FDA guidelines, a manufacturer must comply with all regulations specific to the region or country in which its products are sold.

Depending on the market, food manufacturers may also require additional approvals or certifications, such as NSF Standard 60, which regulates materials used in potable water, Kosher, or organic certification. These approvals/certifications require further raw material restrictions for the water treatment programs and ultimately for the end use manufacturer.

Fruit and Vegetable Processing

The purpose of processing fruits and vegetables is to stop or significantly slow down spoilage, prevent food-borne illness, and maintaining the nutritional value, texture, and flavor. Thermal processing is a method of food preservation, where a food and its container are rendered commercially sterile by the application of heat alone, or in combination with pH adjustment or chemical additives. The hermetically sealed container (cans, glass jars, pouches, and plastic containers) maintains the sterility of the food. Commercial sterility, which is synonymous with shelf stability, means the destruction of all viable microorganisms of public health significance, and those capable of reproducing under normal nonrefrigerated conditions of storage and distribution. Commercially sterile, aseptically processed and packaged foods are also considered thermally processed foods.

There are many different methods to meet commercial sterility criteria, including thermal processing, freezing, aseptic packaging, pasteurization, cooking, and vacuum sealing. Conventional thermal processing involves filling containers with hot or cold food, sealing them hermetically, and heating them in a temperature-regulated vessel, generally called a retort. The heating source may be steam, hot water, or a steam/air mixture.

A different and newer thermal processing method is aseptic processing. The number of systems and the variety of products being aseptically processed are rapidly expanding. This method involves the sterilization of the product and package separately and bringing them together in a sterile environment.

General Process Overview

Prior to being canned, food undergoes a variety of production processes, depending on its type. Vegetables, for instance, are graded, trimmed, washed, and blanched. The latter process inactivates the enzymes present, removes gas from the tissues causing some shrinkage, and softens the tissues, enabling more to be packed into the cans without damage. Whether it is steam generation, cooling, or fluming, water is used extensively throughout fruit and vegetable processing. Water has been the media of in-plant conveyance (fluming) of most fruits and vegetables in this industry segment. Not only has this choice been economical, but it provides additional benefits in prewashing and cooling. However, because of the pollution load that results from fluming, and the focus on water conservation, new methods of conveyance (air, vacuum, and mechanical) are now becoming more common, so washing and rinsing which may require as much as 50% of the total water used in process operations, is a separate step. Grading and sizing are sometimes accomplished simultaneously with washing.

After fruits and vegetables are washed, peels are removed in a variety of ways. Steaming or soaking in caustic solutions is the most common, but air and mechanical peeling are also used. Dry caustic peeling of potatoes is gaining acceptance within the industry as a means of greatly reducing pollution loads.

Water blanching is generally used for vegetable processing to remove air and to leach solubles before canning. Steam blanching of vegetables is usually used to destroy enzymes before freezing or dehydration. The blanching effluent stream contributes a significant portion of the total pollution load in canning operations.

The cans are filled, hermetically sealed, and then thermally processed to sterilize the contents prior to labeling, packing, and final dispatch.

After the sterilization step, cans are quickly cooled with water, causing steam in the headspace to condense, creating a partial vacuum inside the can. If there were to be a pinhole fault in the can seam, this could cause cooling water to be drawn into the can. Both *Salmonella* and *Staphylococcus* have been seen in cans contaminated via this route. This obviously dictates that only disinfected cooling water be used.

Thermal Processing

All types of natural food products (other than fresh food intended for immediate human or animal consumption) must be thermally processed.

The canning industry recognizes two categories of food products: high acid and low acid. The difference is in the degree of thermal processing needed and the influence of final product pH on long-term preservation of the food. Low-acid foods (pH > 4.6) require higher heat processing treatment. Examples of low-acid food products are carrots, beans, peas, meat, corn, and fish. High-acid foods (pH < 4.6), such as berries, sauerkraut, plums, pears, apricots, and tomatoes, require less heat processing, because bacterial spores are already partially inhibited by the low pH.

Hydrostatic Sterilizer

Hydrostatic sterilizers are designed to continuously process food products packaged in a variety of container types and sizes including metal, glass, and plastic containers. These sterilizers are specifically suited for processing products that require long cook and cool times, high throughputs (up to 2000 containers per minute), and from those deriving little or no benefit from agitation.

Sterilizers operate on the hydrostatic principle, with the pressure of saturated steam in the sterilizing zone, balancing heads of water. The temperature prevailing in the sterilizing zone depends on these heads, which are adjustable. The product in the containers is conveyed through the machine in carriers fitted between two endless steel chains. Automatic feed and discharge systems are used to introduce the filled containers to the machine and remove them from the machine, respectively.

Manufacturers of hydrostats claim the following advantages:

- Savings in floor space
- Reduced heating and water costs because of regenerative heating and cooling
- Capability of processing all sizes of cans, glass containers, and pouches
- Constant temperature operation due to hydrostatic control
- Minimal thermal and physical shock to containers because of low chain speed [1–6 ft/min (0.3–1.8 m/min)]

The main disadvantages of hydrostats are the large capital investment required. Also, maintenance costs are relatively high due to a greater number of moving parts. Hydrostats are usually preferred to continuous rotary cookers when the following conditions are involved:

- Year round operation
- When strict temperature control is required (where products may be temperature sensitive, for example, product discoloration at high temperature)
- Filler speed at least 400 cans per minute on consumer sizes

A hydrostatic sterilizer process (Fig. 40.1) generally consists of four stages: a water-filled leg for can preheating; a steam pressurized cooking section called a steam dome where the sterilization process takes place, a water-filled leg for can precooling and a final atmospheric

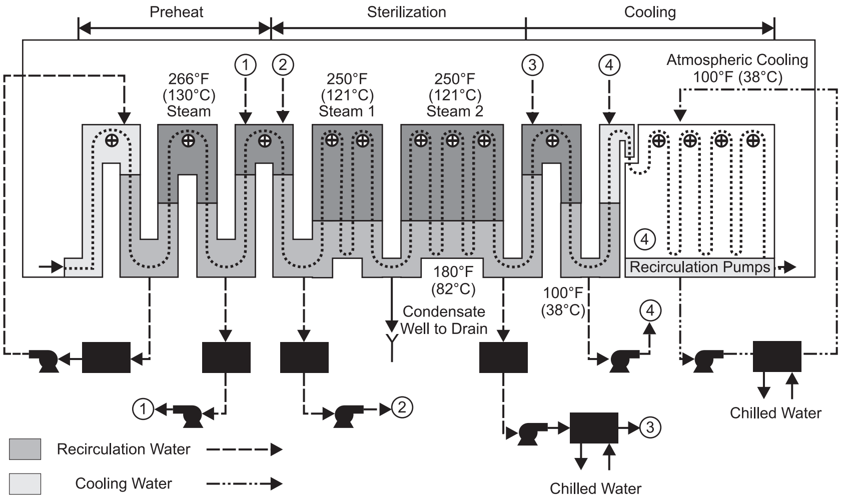


FIGURE 40.1 Hydrostatic sterilizer.

cooling section, usually consisting of a cascade or spray-type cooling tower (not to be confused with a standard evaporative cooling tower). In some cases, an additional pressure cooling zone is required.

Hydrostatic In-Feed Leg (Preheat Section) This section contains a column of water to act as a hydrostatic water valve that allows the entrance of containers into the sterilizing chamber (steam dome) without the loss of pressure and temperature. As the cans are fed into this leg at temperatures of 185 to 194°F (85–90°C), they are exposed to increasing pressure as they pass through the column of water. If no means were taken to prevent it, rapid exposure of the container to processing pressure would crush it. In order to prevent this problem, the water in this leg is heated either by direct steam injection or a heat exchanger. In this way, the contents of the can are heated, and an internal can pressure is built up to withstand the external water pressure.

Sterilizing Chamber (Steam Dome) Cans enter the steam dome where appropriate temperatures of are maintained as required for the specific product being processed. The time containers remain in this section is controlled by both the number of chain passes built into the machine and by chain speed. This depends on the heat penetration characteristics of the product being sterilized. The objective here is to achieve the sterilizing temperature in the center of the can for the predetermined processing time required for complete sterilization.

Hydrostatic Discharge Leg (Precool Section) On discharge from the sterilizing chamber, the internal pressure in the container will be relatively high. With insufficient external pressure it would expand enough to lose the lid. To prevent this, the leg is cooled to ensure that the internal can pressure is reduced gradually and can integrity is maintained. This temperature control can be achieved by:

- Recirculation of water between preheat and precool sections
- Use of an exchanger with cooling water on one side
- Direct cooling water injection into the precool (discharge) leg
- A combination of methods

In some applications, it is not possible to remove the heat quickly enough from the cans during passage through the precool leg. In such cases, a pressure cooling leg is employed where compressed air (air-over pressure) is applied to maintain container integrity until they are further cooled by passage through the atmospheric cooling section (cooling tower).

Atmospheric Cooling Section The final stage of the process is to cool the cans to their final targeted temperature of 95 to 110°F (32–43°C) by making several passes through a series of water sprays or cascading cooling water in the cooling tower section. In some machines, this is followed by passage through an immersion tank (cooling trough) prior to discharge. Due to the possibility of "micro-leakage" of cooling water into the cans, bacteria counts must be maintained at a very low level, usually below 100 CFU/ml. The FDA requires a trace level of a sanitizer (usually chlorine or bromine) to be maintained in the water.

Rotary Horizontal Sterilizer

Rotary sterilizers provide continuous container handling with intermittent container agitation. These systems employ one or more processing shells for sterilization and one or more cooling shells depending on the product and process conditions. They are designed to take sealed containers continuously from the seamer equipment through the sterilizing and cooling operations. The rotary shells can be arranged in various configurations which may include preheating and/or pressure cooling shells in addition to the atmospheric cooling and sterilizing shells (Fig. 40.2).

Most of the rotary sterilizer shells are 58 to 112 inches (1.47–2.84 m) in diameter and vary in length from 15 to 52 ft. (4.6–15.8 m). Although variations can be found based on differing processing needs, the length required is dependent on the process time, production speed,

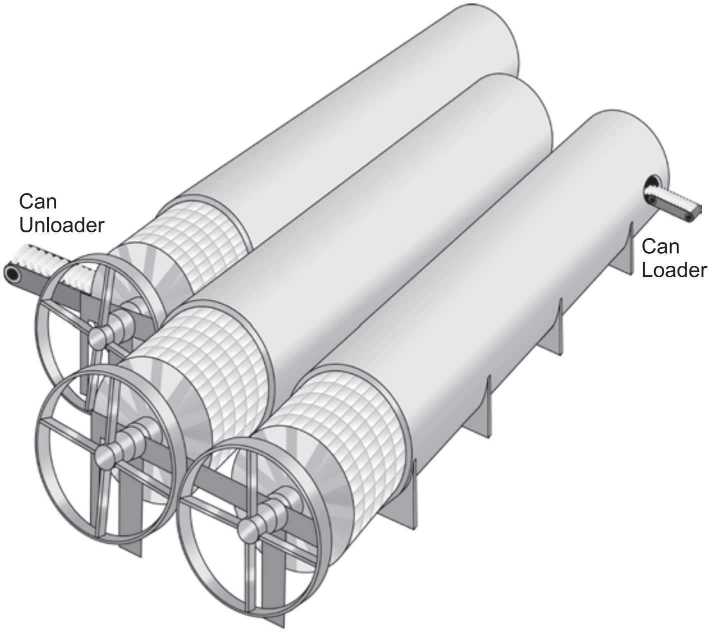


Figure 40.2 Rotary horizontal sterilizer.

and container size. Some models can operate at process temperatures as high as 292°F (144°C) and some at line speeds of 800 containers per minute.

Rotary sterilizers can be either pressurized or atmospheric. In pressurized sterilizers, steam is injected directly into the cooking shell. Steam is used in the cooking shell and in pressure cooling shells (directly injected to the water to control pressure and temperature), and water is used in the pressure and atmospheric cooling shell. For atmospheric cookers, water in the cooker shell is heated through direct steam injection or by recirculating the water through a heat exchanger. Atmospheric cookers are normally found only in vegetable and fruit processing facilities.

Inside the cylindrical processing shell is a rotating reel with "angles" to hold the containers. A fixed spiral "*T*" is permanently attached to the inside of the shell. The turning of the reel and the lead of the spiral *T* move the containers through the length of each shell.

As the containers advance through a sterilizer shell, they are subjected to a targeted temperature, which sterilizes the contents. The target temperature will vary depending on the product. When the containers reach the end of the processing shell, they are transferred to a cooler shell.

Continuous cooling can be accomplished in an atmospheric cooling shell, a pressure cooling shell, or both. Depending on the product, container size, and processing temperature, the pressure cooling may be necessary to prevent buckling of the containers (Fig. 40.3).

Continuous rotary sterilizers offer several advantages over still retorts. One advantage is the reduced process time due to intermittent agitation. The agitation occurs when the containers roll on the bottom of a shell, resulting in product movement within the container. This movement increases the rate of heat penetration. The product agitation allows the use of high processing temperatures, and in some instances, product uniformity and quality are improved. Another advantage is the possibility of reduced production costs through savings in labor cost and steam consumption.

Some of the possible disadvantages associated with continuous rotary sterilizers include the initial and the fact that each system will accommodate only a limited range of container sizes.

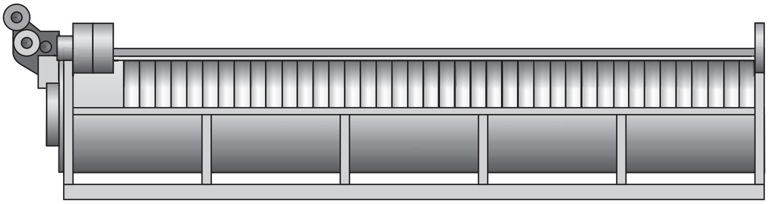


FIGURE 40.3 Rotary pressurized cooler.

Still Retorts

Retort sterilizers (often referred to as still retorts) work in a batch operation, with the cans normally held in carts or baskets. These systems use one processing shell for both cooking and cooling. They are designed to process sealed containers either stacked in layers separated by plastic divider sheets or simply dumped in metal baskets. In this process, the cans remain in the same shell for both the cooking and cooling processes.

All still retorts are of the pressurized type, but the method by which the cans are heated and cooled may vary. There are two distinct ways heat can be exchanged to cans in a retort sterilizer. The first is by direct steam injection, where the steam is distributed in the retort by means of steam manifolds. The second is by exchange of a recirculated body of water in the retort heated and cooled through a heat exchanger. The major difference between these two methods is that with direct injection of steam, there is very virtually no water in the retort during the cook cycle (only a small amount of accumulated condensate) when operated properly. When a heat exchanger is employed, there is water in the cooker throughout multiple cycles. This type of retort is sometimes referred to as a "Sterile Water" retort. Some retort systems utilize direct steam with retained cooling water cooled via a heat exchanger interfacing with an external cooling tower.

The cook cycle time period will depend on the size of the cans and the product being processed. Once the sterilizing process is completed, the steam is shut off.

Following the sterilization cycle, cooling water is either admitted to the retort (in direct steam injection-type systems) or circulated through a heat exchanger which is utilized throughout the duration of the cooling cycle. During the cooling cycle, air or steam pressure must be employed to allow for gradual external pressure reduction to counter the internal pressure of the cans while they cool. This prevents the cans from over-expanding and becoming misshapen or leaking. Since the water in "Sterile Water" retorts often remains in the machines for long periods of time, accumulation of product in the water or breakdown of water treatment chemicals must be considered when designing chemical programs.

A commonly used variation in the batch system is the Immersion Retort. These units utilize a water-cook system where recirculated water is heated via direct steam injection. The containers being processed are held in baskets which are rotated in the machine to agitate the contents. The cook water is dispensed from a holding tank normally located on the top of each unit (some systems utilize a common tank for a given number of retorts). This water is held at a high temperature between sterilization cycles to allow for more efficient processing.

The cooling cycle in Immersion Retorts has two phases. The first brings in cooling water (sometimes fresh makeup water) which displaces the hot water to the holding tank allowing some of the cooling water to migrate to the hot water vessel. After the first phase, the cooling water circulates through the lower drum with the baskets continuing to rotate. The cooling water temperature is controlled with a temperature control valve assembly that lets the cooling water enter and exit the lower drum or with a plate and frame heat exchanger interfacing with external cooling water.

The advantages of still retorts over continuous rotaries include:

- Lower capital cost
- Greater flexibility in container size due to carts as opposed to angles and flights in rotaries and hydrostats
- Equipment easier to monitor and control

The major disadvantages of still retort sterilizers are longer processing time due to lack of agitation and extra time associated with loading and unloading the retort and the amount of steam that must be vented in order to remove all the oxygen from the vessel at the beginning of the sterilization cycle.

Table 40.1 compares the steam and cooling water usage for the three types of retorts used in the food industry.

Containers

The most common containers are steel cans. Steel cans used in food packaging are usually made of electro-tin plate steel (ETP) or tin-free steel (TFS). Organic coatings such as vinyl, epoxy, or enamel are used to protect both the inside and outside of all TFS cans. Tin cans typically require these coatings on the inside and sometimes the outside to protect the base metal from corrosion.

A trend toward reduced tin weight and changes in the chemistry of the organic coating as well as an increasing use of easy-open ends puts a far greater pressure on correct water treatment to maintain good container appearance and integrity.

Type of Equipment		Steam Use lb/lb (kg/kg) of Product	Cooling Water Use gal/lb (L/kg) of Product
Still retort		0.3–0.4	0.6 (5)
Rotary sterilizer	Pressurized	0.15–0.2	0.2–0.3 (1.7–2.5)
	Atmospheric	0.3	0.2–0.5 (1.7–4.2)
Hydrostatic sterilizer		0.12–0.15	0.1–0.2 (0.8–1.7)

Table 40.1 Typical Steam and Cooling Water Requirements for Various Types of Sterilizers Equipment

Other types of packaging are also thermally processed. Aluminum cans, glass jars, glass or plastic bottles, plastic trays, and flexible pouches are other types of food containers that are becoming increasingly popular.

Water Treatment Objectives

Specific challenges found in processed and canned food plants include the following:

- Food safety
- Container appearance
- Equipment protection
- Sustainability
- Wastewater

Food Safety

Poor microbiological control in sterilizer cooling water is one of the primary causes of product spoilage. Best Practice calls for total bacteria counts to be maintained at less than 100 colony forming units per milliliter (CFU/ml). This is a challenging task as there is always a varying amount of contamination from lubricants and food product in this water. Unfortunately, the high halogen demand often employed to control bacteria in this water and relatively high temperatures can be corrosive to the equipment, particularly in the vapor space, and cans.

Container Appearance

The primary objective of a water treatment program in sterilizer systems is to minimize container spotting and staining due to equipment corrosion byproducts, organics in the water or mineral salts deposition. Most companies have a low tolerance for container spotting as it hurts “shelf appeal” for their products in the super market. Also metal cans may rust later in storage as a result of the hygroscopic nature of mineral or organic deposits on cans.

Another concern is that excessive deposits (scale and corrosion products) inside the equipment can actually block the pathway of the containers, in particular on rotary cooker spirals, and may scratch or dent the metal surface of cans. Once scratched, the container is more likely to experience postprocessing corrosion.

Can shelf life is a major concern for companies that maintain a large inventory of product that may ship to customers a relatively long time after it is processed. This is of also a concern for products intended for export, as corrosion, that can accelerate during overseas transit, may negatively impact the integrity of metal containers. There have been examples of entire shipments of cans refused by Asian customers, due to the presence of a very minor corrosion on cans.

It is important to be aware that lubricants are used to protect equipment and maintain smooth operation. Varying levels of these lubricants will be found in retort cooling water. This can leave a film on cans, making labeling difficult. With a well-designed water treatment program including the correct surfactant treatment, this film can be minimized.

Equipment Protection

The second most important water treatment objective in Thermal Processing plants is to prevent scale and corrosion in the processing equipment. Unplanned equipment failure during the season is very costly not only in the capital cost of repair but, more importantly, in production loss. Seasonal plants generally run 24 hours a day, seven days a week, and cannot afford any downtime. The cost of inadequate protection of sterilizer systems is a long-term depreciation problem affecting plant equipment amortization and capital plans.

A hydrostatic sterilizer can cost as much as 8 to 10 million U.S. dollars (chain replacement is typically over 1 million U.S. dollars with several months lead time for delivery). A Rotary sterilizer shell costs anywhere between 0.3 and 1 million U.S. dollars. Even though the equipment life is generally over 30 years, moving parts and “wear parts” such as chains, frames, chain guides, and rails are more directly affected by corrosion and scaling problems, leading to costly repair or replacement.

Sustainability

Most companies today are deeply concerned with sustainability in their factories. The cost of water both incoming and discharge is rising rapidly on a global basis. Also companies are increasingly concerned with their plant operations impact on the environment due to pressure from their customers who require documentation of the implementation of “green projects.” Recycling and heat recovery projects tied to sterilizer operations are great opportunities for impressive reduction in water and energy consumption. It is important that such project planning include the impact on water conditions as they tend to increase the holding time of contaminated process water. Proper filtration and offline cleaning and sanitation procedures must be included in such projects. Failure to do so will negatively impact container appearance and, more importantly, the ability to maintain low bacteria levels in the cooling water systems.

Wastewater

As with all other industries, food processors are now forced to reduce the pollutant loading of their effluent water. This pollution loading varies enormously from one type of product to another. For example, in the processing of asparagus, the biochemical oxygen demand (BOD) and suspended solids are usually below 100 mg/L, whereas in the production of whole kernel corn, the BOD and suspended solids may be several thousand milligrams per liter. The solid wastes also vary considerably from one product to another.

Although many canneries are served by municipal sewage systems, a growing number operate their own waste treatment facilities. Those in farm areas where land is available have been successful in using spray irrigation as a means of disposal reducing the volume of water requiring treatment. However, changing environmental protection agency (EPA) regulations have reduced the volume of water that can be used in such applications. As a result, the demand for improved wastewater strategies has greatly increased.

Meat and Poultry

A packinghouse for beef or pork slaughtering will include holding pens for the animals, a kill floor, chilling coolers, and shipping facilities. There may be an inedible/edible rendering department, a hide cellar, and facilities for processing other by-products such as blood. The process is continuous, with animals entering in a steady stream in one end and product leaving at the other.

Live poultry are unloaded at the processing plant onto a moving chain and then taken to the killing station. The birds are then scalded with hot water to remove the feathers, assisted by mechanical beaters and manual pulling. Residual hair and feathers are singed off with a flame or by wax stripping, and the birds are then surface washed. The birds are eviscerated manually and washed internally and again externally. The carcasses are then chilled or frozen, packaged, and shipped to market.

Water Needs

One of the key water needs of the meat packing industry is centered around a requirement for reliable quantities of 140°F (60°C) and 180°F (82°C) “on demand” potable hot water. Internal deposition in the potable water system is likely. The three main causes of potable water system problems are:

1. Heat exchanger, direct steam/water heater, or hot water delivery lines scaling and being unable to produce enough hot water at the use point.
2. Chips and scale from the heat systems or water distribution system breaking off and depositing on the carcasses or meat being processed.
3. Contamination of the meat products due to “red water.” This results from iron deposition in any point of the system being sloughed off and making its way to the processing lines.

All chemicals used in and around meat packing plants require regulatory approval. The approval may vary based on the process area or plant hazard analysis critical control point (HACCP).

Primary boiler steam load is for the operation of water heaters required for the 140/180°F (60/82°C) water systems. Hot water heat exchanger condensate is normally returned. If the plant has rendering cookers, they are typically operated at 20 to 30 psig (138–207 kPag), and condensate may be returned. If returned, contamination by grease can be an issue.

Defoamers

Defoamers are used in processes such as scalding water, wastewater, washing water, dehairing systems, rendering cookers, and protein recovery. Excessive foam may cause production slowdowns and increase the risk of product contamination. As a rule, defoamers should be FDA or USDA approved.

Ammonia Compressor

This unit is the heart of most meat processing cooling water systems. Warm ammonia gas comes to the compressor from the coil cooling units located throughout the plant. The compressor compresses this liquid into a superheated gas. The gas then travels to the shell-and-tube heat exchanger or the evaporative condenser, where heat is exchanged from the ammonia and the gas becomes a liquid. The liquid drains to an accumulator and is available to be sent back to the coil units, where it removes heat (and thus cools) by becoming a gas.

Major meat processing plants typically have a number of ammonia compressors, often specifically designated to certain plant areas, and staged on and off through computerized controls based on suction side head pressures.

A special type of system is found in a meat plant that practices rendering. This shell-and-tube rendering vapor heat exchanger, transfers the waste heat of the process vapors to the incoming process water. This system needs to be carefully monitored, because high and varying temperatures from the rendering cookers can cause deposition.

Odor Control

Odor control chemical additives can be grouped based on their mode of action. These include:

- Masking agents, deodorants, and perfumes
- Counteractants
- Oxidants and other microbiocides
- Enzymes or biological augmentation
- Chemical precipitants and scavengers

Biofiltration is an odor treatment process, where contaminants and odor causing agents are adsorbed and filtered through biologically active media compost. The main by-products of the breakdown are water and carbon dioxide. Biofilters are extremely effective when they are well managed, and can reduce odor emissions by 90%, hydrogen sulfide by 85%, and ammonia by around 50%.

Gas Scrubbers

The most commonly used scrubbers in the meat processing industry are preformed spray, packed bed, multistage wet scrubbers that are very effective for high intensity odor control. The plants use Venturi scrubbers to remove coarse solids loading before treatment in the primary multistage unit. Plants may treat process and fugitive emissions by ducting the plant ventilation air through a single-stage wet scrubbing system, in order to minimize odorous emissions. More plants are considering polishing scrubber exhaust with biofiltration.

Rendering

Rendering and waste product utilization are major factors in the economics of meat processing. Rendering plants process animal by-product materials for the production of tallow, grease, and high-protein bone meal. Plants that operate in conjunction with animal slaughterhouses or poultry processing plants are called integrated rendering plants.

Plants that collect their raw materials from a variety of offsite sources are called independent rendering plants. Independent plants obtain animal by-product materials, including grease, blood, feathers, offal, as well as entire animal carcasses. These materials come from butcher shops, supermarkets, restaurants, fast-food chains, poultry processors, slaughterhouses, farms, ranches, and feedlots.

Wastewater

Waste treatment systems in the meat packing industry and in further processing plants are used to remove suspended solids, oil and grease, blood, and BOD from the effluent water before discharge to a receiving stream, a publicly owned treatment works (POTW), or for agricultural irrigation use. Wastewater from slaughterhouses and packinghouses contain organic matter (including grease), suspended solids, and inorganic material such as phosphates, nitrates, nitrites, and salt.

Most meat processing plant wastewater treatment consists of equalization followed by dissolved air flotation (DAF) and some type of secondary biological system. Sludge from the DAF and biological system is then pressed or dried and disposed of via land application, landfill, or recycled to recover nutrient value. Recycling of DAF sludge requires the use of generally recognized as safe (GRAS) sanctioned polymers.

In older plants, located in the countryside, the secondary system is often a simple aerobic pond or anaerobic lagoon, followed by discharge of the water for irrigation use. The ponds are then dredged on a frequent basis (2–3 years) and the sludge dried before being land applied. In newer, modern plants, the secondary system may have a clarifier to process the spent biomass.

The Beverage Industry

The beverage industry is a major consumer of water, much of which becomes part of the final product. The balance is used for clean-in-place (CIP) operations, pasteurization, container warming or cooling, cooling of compressors and refrigeration equipment, and makeup to boilers producing steam used for cooking, evaporation, heating of pasteurizers, and space heating.

The water used in the product must, of course, be potable; in addition, the water quality can have a significant impact on the taste of the finished beverage. In the soft drink industry, for example, it has been historically common practice to lime soften the water for hardness and alkalinity reduction. However, membrane filtration processes, such as ultrafiltration (UF) and reverse osmosis (RO), are gradually replacing lime softening. In many facilities, the water is passed through activated carbon for the removal of chlorine and residual tastes or odors due to organic contamination. Most soft drink bottling plants have boilers to provide the heat required for CIP operations and potentially for bottle molding operations.

Bottled water is a large portion of the overall beverage market. There are many different types of bottled water operations. This includes facilities that bottle spring water and plants that simply bottle processed city water. Unit operations vary depending upon the company and the water source. However, it is common to see media filtration, carbon filtration, and membrane filtration. The goal is to provide water that is free of microbial and taste contamination. Regulations regarding the allowable concentration of specific contaminants in water are detailed and growing every year. Many of these facilities make their own plastic bottles. This typically involves blow-molding operations, which require heating (steam) and cooling with closed and open recirculating cooling loops.

Breweries, fruit juice bottlers, and distilleries operate their own steam plants, because steam is required for cooking raw product and pasteurization, and is the energy source for distillation and evaporation. Breweries generally pasteurize or warm the beer once it has been placed into containers (bottles or cans). This operation requires steam and cooling water. An increased emphasis has been placed on reducing overall water usage in every brewery. By 2007, the average water usage was five liters of water for every liter of beer produced. The unit operations in breweries and distilleries are quite similar to those found in the chemical industry in principle, but special designs enable the process equipment to be readily cleaned to prevent microbial contamination of the product, and to avoid risks to the public health.

Special designs of piping and fittings, such as long-sweep pipe elbows, are used throughout the food industry because of this need for sanitation (Fig. 40.4). Highly polished stainless steel, Monel, or chrome-plated steel eliminates scratches, nicks, and crevices, which could offer a home for bacterial growth. The careful cleaning of equipment after each use creates a special problem of pollution control in that spent chemical cleaners, especially those containing biocides, often interfere with the performance of pollution control equipment.

Two water-using systems are unique to the food industry and found in the beverage market: the bottle and container washing systems and the pasteurizer.

Figure 40.4 Typical filter installation in the food and beverage industry. Note the use of special stainless steel piping and fittings. (*Courtesy of Croll-Reynolds Engineering Company, Inc.*)

In the bottle washing operation, both cleaning and sterilization are required, and detergents and biocides are applied to match the severity of the problem. If the bottle washer is handling returnable bottles, it is important to use effective cleaning chemicals, since there is no way of knowing what might have been in the bottles when in the hands of the public. Typical cleaners are a mixture of sodium hydroxide and surfactants or chelants. Because of this, it is beneficial to have softened water for washing and rinsing, as this reduces the demand for detergents and greatly facilitates the drainage of the bottle after rinsing for spot-free surfaces.

When strongly alkaline cleaners are used, these provide a biocidal effect that depends both on the length of time the chemical is in contact with the bottle, and the causticity of the cleaning solution. Even with this protection, however, chlorine is often applied to the final rinse water to ensure sanitation.

In the tunnel pasteurizing operation, as practiced in breweries, the bottled product is moved through the pasteurizer to halt the growth of specific spoilage organisms. A controlled temperature water bath then slowly brings the beverage to approximately 140°F (60°C), and holds it for the required time to ensure that the entire contents of the bottle have been pasteurized. Multiple heating and cooling stages are used to prevent thermal shock to the product and container breakage. The goal for the final product temperature is to reduce it as much as possible without dropping below the dew point. If the container sweats, difficulties arise in the packaging operations. The temperature in the pasteurizing section is maintained by circulating hot water, and the chilling sections may be tied into a cooling tower and supplemented with a closed chilled water system (Fig. 40.5), although once-through cooling water is still widely used.

In the event of bottle breakage, these water systems are inoculated with nutrients (the beverage), and microbial activity may quickly get out of hand. Common industry practice is to utilize chlorine or bromine treatment programs to keep this under control.

For the most part, beverage industry wastewaters are handled by municipal sewage systems. This may require the plant to install equalization facilities to unify the composition and flow rate and to adjust pH. In-house handling of strong wastes, such as chemical cleaners, may be necessary to make the equalization program effective.

A number of large breweries and distilleries operate their own waste treatment facilities. While conventional biological treatment had been the norm for many years, the last 15 years has shown a significant increase in the use of anaerobic pretreatment. The BOD loading in brewery waste is significant. This leads to high sludge volumes and high disposal costs. With BOD levels consistently at 2500 mg/L or above, brewery waste is ideal for operating anaerobic pretreatment facilities.

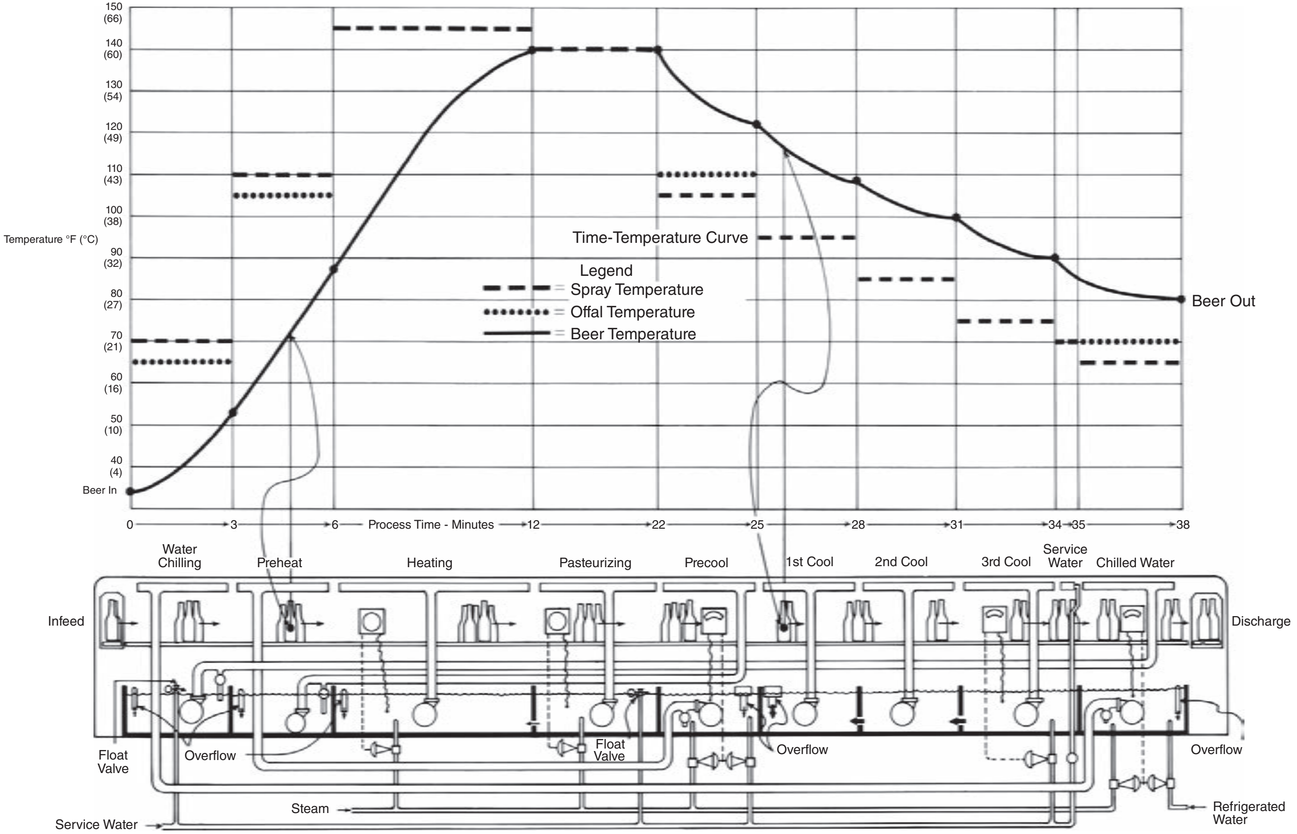


Figure 40.5 Flow of product and water through a pasteurizer for careful control of beverage temperatures. Flows are cascaded for energy recovery. (*Courtesy of Barry-Wehmiller Company*.)

The Sugar Industry

There are many process steps in the sugar industry (some of which are similar to corn processing). As the largest food processing water user with a variety of process operations, the sugar processing industry offers a good example of water use in food processing.

Sugar (sucrose), a chemical classified as a disaccharide with the formula $C_{12}H_{22}O_{11}$, is derived from two major crops: sugar cane and sugar beets. Cane is cultivated in tropical and semitropical climates (Louisiana, Florida, Central America, and Brazil), while beets are raised in temperate climates (North Dakota, Minnesota, Montana, Michigan, Wyoming, Nebraska, Colorado, Idaho, and California). 51% of the U.S. sugar produced from beets comes from the Red River Valley which is in eastern North Dakota and western Minnesota.

Cane exceeds beet sugar production but in the United States 55% of total sugar production comes from sugar beets. Because these crops spoil rapidly, they cannot be stored for extended periods unless they are frozen, and the production of sugar is seasonal, with a mill operating a production campaign of about 120 days geared to the plant harvest. However, facilities that freeze the beets the production campaign are about 250 days. Sucrose, which constitutes up to 20% of the weight of the cane or beet, is readily degraded by bacterial action. The first step in the degradation is the production of invert sugars (fructose and glucose):

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}} + H_2O \rightarrow \underset{\text{fructose}}{C_6H_{12}O_6} + \underset{\text{glucose}}{C_6H_{12}O_6} \tag{40.1}$$

The second step is the production of lactic acid ($C_3H_6O_3$) under the conditions prevailing in beet sugar manufacture, or dextran ($nC_6H_{10}O_5$) under the conditions common in cane sugar mills. Since bacteria primarily cause this degradation, it is important to maintain control of microbial organisms throughout the mill to avoid loss of sucrose production. Microbial activity also causes processing difficulties, such as filter blinding, slime formation, and odors.

Figure 40.6 shows a basic flow diagram for cane and beet sugar processing.

As the crops arrive at the mill, they contain soil and trash accumulated during the harvesting operation. In the case of cane sugar harvested by pushers (similar to bulldozers), the refuse may constitute as much as 10 to 25% of the weight of material delivered to the mill. This is not merely inert material; it represents a major source of bacterial inoculation, since soil organisms are present with appreciable fecal matter from birds, rodents, and other small animals that live on the croplands. Because of this, washing is a critical operation to the preparation of raw materials going to further extraction processes.

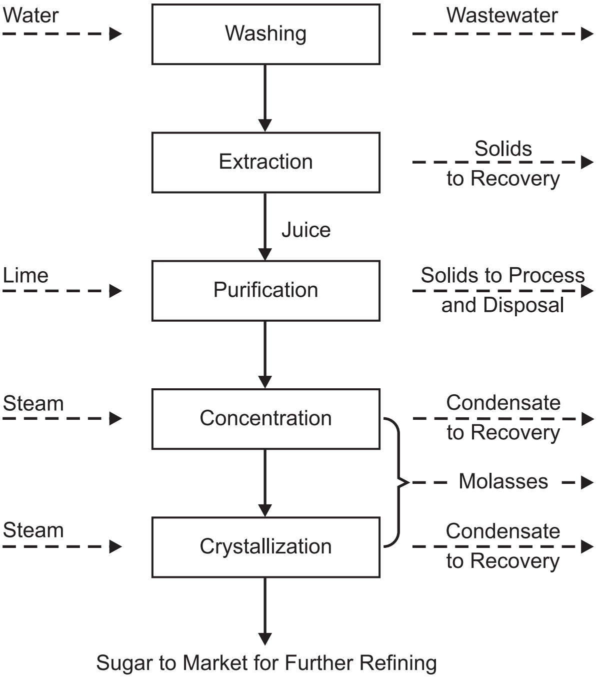


Figure 40.6 Sugar processing flow sheet.

However, washing should not be excessive, as this leads to loss of sucrose in the wash water.

After washing, sucrose is extracted from the raw material. In cane sugar mills, this is usually done by crushing and milling the washed, cut cane stalks, producing a juice containing approximately 12 to 15% sucrose. In the beet sugar industry, the beets are sliced into long, narrow pieces, and the sucrose extracted by washing with water in diffusers at about 160°F (71°C). There is growing interest in the use of diffusers in place of crushers and mills in cane processing to reduce maintenance costs and improve yield.

The cane stalks are pressed after initial crushing and milling to reclaim as much sugar as possible, and the remaining solids (called bagasse) are usually burned in boilers to generate steam. Bagasse may also be used as a raw material for such products as insulation board or acoustical tile. In the beet sugar industry, the beet pulp residue is quite high in protein, and it may be mixed with some of the plant production of molasses for cattle feed.

As with most other natural products, there are a variety of chemicals other than sucrose in the cane and beets. These must be removed to maximize the yield of sugar, minimize the production of molasses, and reduce taste, color, and odor-producing impurities. Lime is used to precipitate these impurities, and conventional separation devices remove the lime mud. The mud is washed to reclaim as much sugar as possible, and it may then be:

- Used to produce fresh lime
- Returned to the fields for its fertilizer value (it often contains significant phosphate)
- Sent to landfill

The purified juice must be concentrated to produce thick syrup, the form of sugar often used by the beverage industry, or to produce a crystalline product. The juice is concentrated by evaporation. Since it contains calcium from the lime treatment, a common problem is the formation of scale in the pans (simple steam-jacketed evaporators) or in the multieffect evaporators. Another common problem is foaming, as the juices become concentrated during evaporation.

The flow sheet of a cane sugar mill producing raw sugar is shown in Fig. 40.7. There is widespread use of steam throughout the plant, so the boiler house is a significant factor in economical production of sugar. Many sugar mills operate intermediate pressure boilers and produce electric power, taking extraction steam from the turbines for operation of pans, evaporators, and crystallizers, and in many cases taking part of the steam through the turbine generator to a condenser. Cooling water from both turbine and evaporator condensers may then be used as process water.

Because the operation of a multieffect evaporator produces more water as condensate than it consumes as steam, there is usually an excess of condensate available as boiler feedwater. This condensate often presents special problems in that it is likely to be high in ammonia, and it may periodically contain sucrose or invert sugar. The introduction of sugar into the boiler quickly produces an acid condition, and careful monitoring of the condensate system for sugar content is important to the protection of the boiler system.

The pollution control problems of the sugar mills are unusual because of the seasonal nature of the industry. The campaign is usually during the dry months, when streams cannot assimilate excess organic loading. The mills minimize discharge flows by recycling as completely as possible, and the wastewaters are treated biologically and impounded for solar evaporation or controlled discharge, when stream flows return to acceptable rates.

The Grain, Oil Processing, and Biofuels Industry

This industry segment consists of corn wet milling, wheat processing, oil processing, and biofuels. Each will be discussed separately.

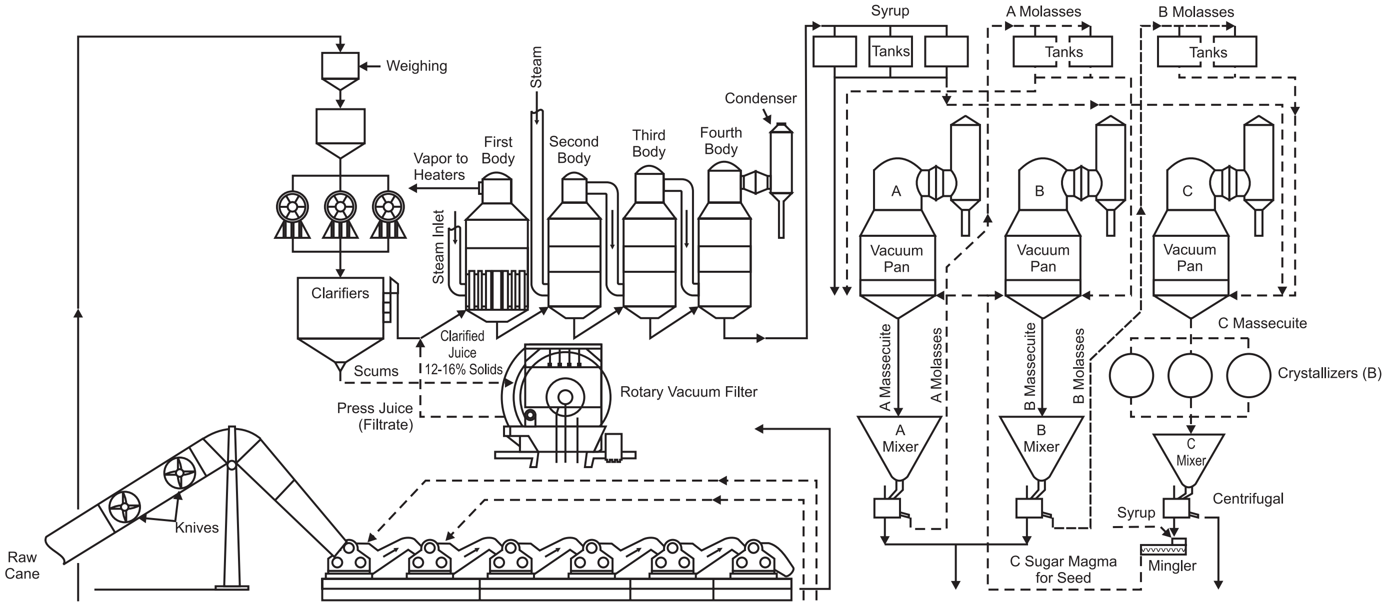


FIGURE 40.7 Process flow chart of cane sugar mill. (*Courtesy of Rio Grande Valley Sugar Growers, Inc.*)

Corn Wet Milling

Corn refining began in the United States in the mid-19th century, with the development of the process for cornstarch hydrolysis. Before this time, the main sources for starch were wheat and potatoes. In 1844, the William Colgate and Company wheat starch plant in Jersey City, N.J., became the first dedicated cornstarch plant in the world. By 1857, the cornstarch industry reached significant proportions in the United States. Starch was the only product of the corn refining industry. Its largest customer was the laundry business.

Today, starch, glucose, and dextrose are still core products of the wet milling industry. However, the products of microbiology (fructose, ethanol, food additives, and chemicals) have overshadowed them. New technology and research have significantly expanded the industry's product portfolio. Advances in process engineering and biotechnology have enabled refiners to become low-cost suppliers of basic food and chemical ingredients, opening new markets in the food and industrial sectors. From one bushel of corn, a producer can get:

- 32 lb (14.5 kg) of starch
- 11.4 lb (5.2 kg) of gluten feed
- 3 lb (1.4 kg) of gluten meal
- 1.6 lb (0.7 kg) of corn oil

The wet milling process is broken into seven primary parts:

1. Cleaning
2. Steeping
3. Germ recovery
4. Fiber recovery
5. Gluten (protein) recovery
6. Starch washing
7. Co-product manufacture

In the mill, a series of solid/solid separation steps, separate the fiber, gluten, protein (germ), and starch from a signal kernel of corn. The oil is extracted from the germ and is sent for further processing. The starch is then moved to the refinery, where a multitude of products can be made. Over the past couple of decades, major developments of the industry include:

- Ethanol as a motor fuel
- High fructose corn syrup (HFCS) reaching a near par with sugar consumption
- Specialty sweeteners such as crystalline fructose

- Food and feed additives such as vitamins, lysine, tryptophane, and others
- Organic acids for industrial and food use
- Degradable replacements for chemical products

As the name suggests, the wet milling industry is an extremely water intensive process [30–40 gal (114–151 L) per bushel of corn ground, where a bushel is 56 lb (25.4 kg)]. This process is the largest user of energy and water in the food industry. It is within the mill (Fig. 40.8) where the majority of the water and energy is used. Balancing the water use in this process can be challenging. Freshwater enters the process to rinse the pure starch, and flows counter-current upstream to be used for washing various co-products, until it reaches the front of the mill where it is used for soaking the corn. This process is called steeping, which acts as an antimicrobial and prepares the kernel for the physical separation steps that follow. As the various co-products are separated, they need to be dried, and the water that was put into the process now needs to be removed through multieffect evaporation, as well as by natural gas and steam driven dryers.

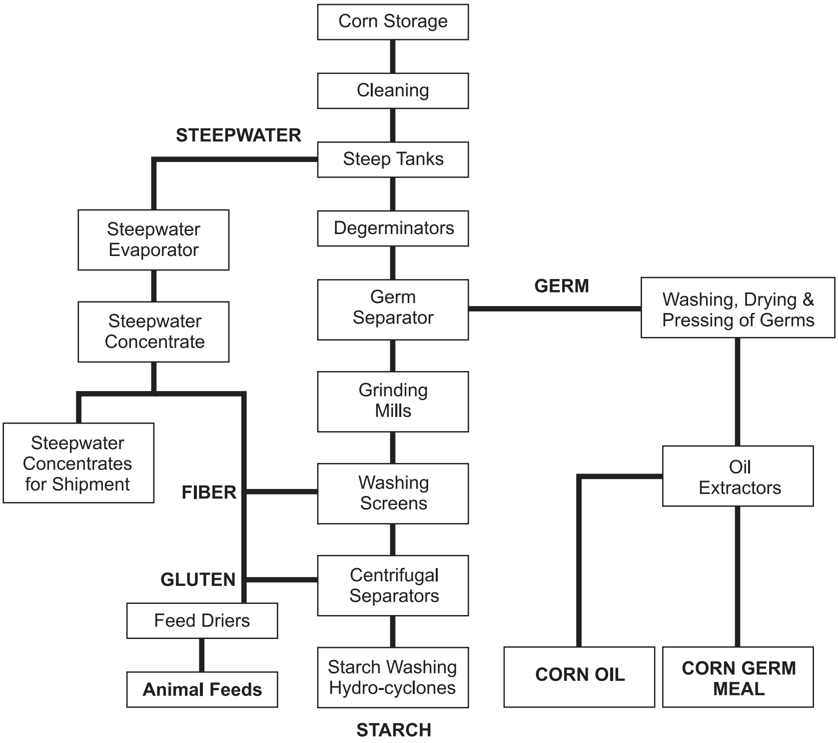


FIGURE 40.8 Wet corn milling process.

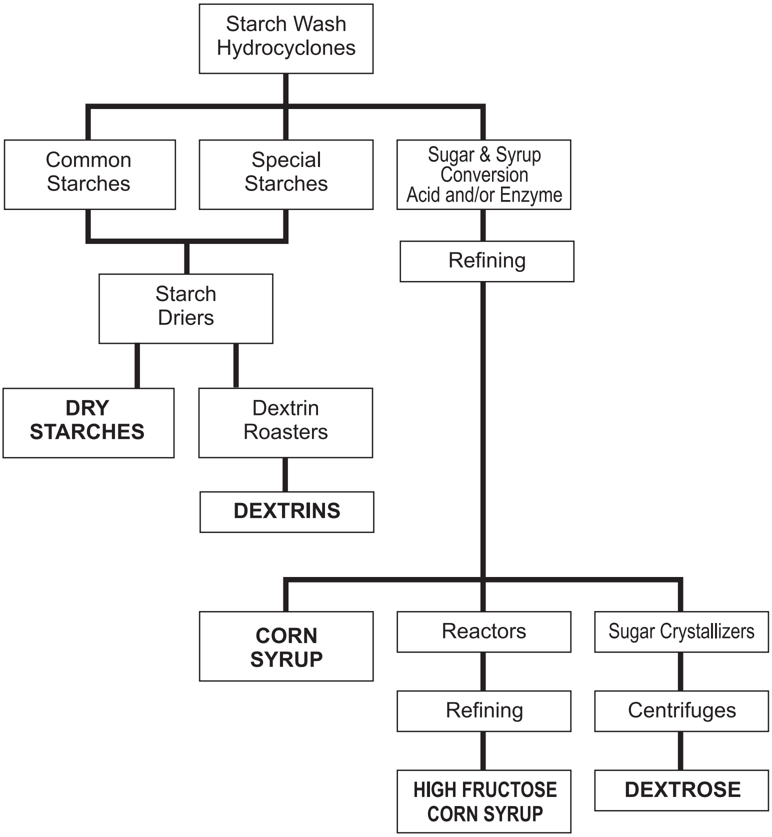


Figure 40.9 Starch refining process.

After the starch is extracted via the milling process, it is further processed into a variety of products. The standard starch refining process is shown in Fig. 40.9.

The steam and cooling water systems that provide the necessary heating and cooling requirements are intensive and require chemistries to inhibit corrosion, scale, fouling, and microbiological activity. In addition to the utility systems, other technologies can be applied, including process deposit control, foam control, and fuel additives to treat the end ethanol.

Wheat Processing

Wheat continues to be processed for its starch and gluten components. However, the process is quite different from that of corn milling (Fig. 40.10).

The wheat is first dry milled by grinding and sieving to separate different fractions depending on size, and the bran and germ are thus

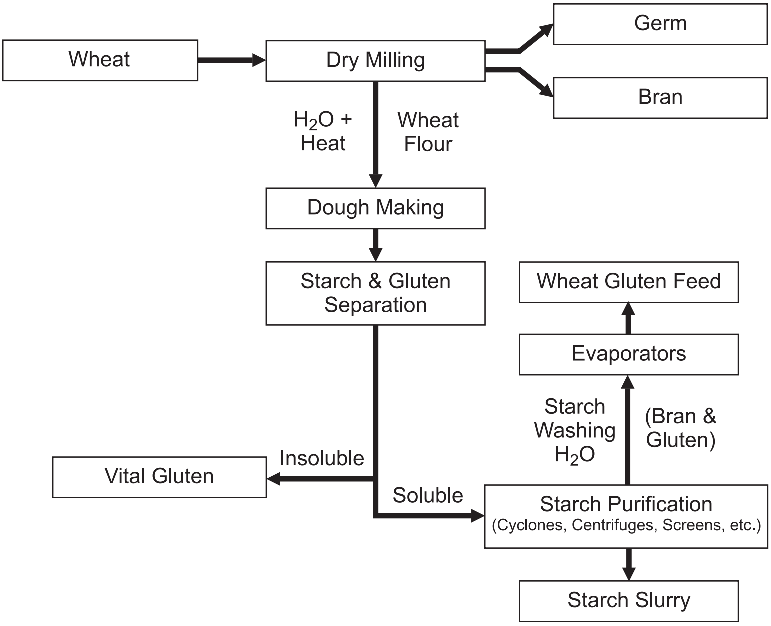


FIGURE 40.10 Wheat processing.

separated from the wheat flour. Wheat flour is then suspended in water and sheer and heat is applied to create dough. Through this process, the gluten (protein) coagulates. The gluten is separated on a screen, dewatered, and dried. What remains is the starch. Purification is completed by removal of fiber and pentosans in a number of washing steps including hydrocyclones, centrifuges, and screens. The wash water still has high amounts of gluten in it and is recovered through multieffect evaporators. Residual pentosans, if not removed properly or cleaned frequently, can cause major scaling in these unit operations. The concentrated gluten is then dried as a final product.

Water and energy uses are much lower in the production of wheat products versus corn wet milling, as there are not the large amounts of water added to the process. Therefore, the amount of energy needed to drive that water off the end products is much smaller. Cooling towers, boilers, and evaporator systems exist within this process and experience similar problems mentioned earlier, if not properly treated.

Oil Processing

Edible oil processing has a more global reach than any of the other grain processing operations. Oil processing has operations in every corner of the globe. There is a variety of oil processes, depending on the seed being used. The water use is about 50 to 60% less than that of the corn wet milling industry at 10 to 20 gal (38–76 L) per bushel [56 lb (25.4 kg)]. As in most of the processes already discussed, there is a preparation of the crude raw material, before it is made into food products (Fig. 40.11). This preparation consists of milling, drying, and oil extraction. The oil seeds are cleaned and dried and are then passed to cracking rolls to remove hulls. Steam jacketed cookers (called conditioners) are used so that the oil seed can be flaked in the case of soybean, or pressed for partial oil extraction in the case of sunflower and rapeseed (canola). Dry steam is critical in these processes, as it can affect oil seed moisture content and slow drying and overall production. About 10 to 30% of the steam is used here.

The flaked or pressed oil seeds are then passed to hexane extractors. In most cases, percolation extractors are used, where hexane is passed over the bed of flakes. A mixture of oil and hexane percolate down through the bed, and flakes leave containing 35% hexane, 8% water, and 1% oil. The hexane is then stripped from the wet flakes through a desolventizer-toaster. The remaining solid material is made into meal for animal feed. The hexane-oil mixture is passed through flash evaporation, vacuum distillation, and steam stripping to remove the hexane. A critical key performance indicator is the amount of hexane that is recovered. About 1 to 2 gal (3.8–6.9 L) of hexane is lost per ton (tonne) of oil processed. Cooling efficiency is vital to ensure that proper amounts of hexane are recovered. The crude oil is then sent on for further processing. This is can be done on the existing site of the mill, but in many cases, the oil is degummed and sent to an oil refining facility.

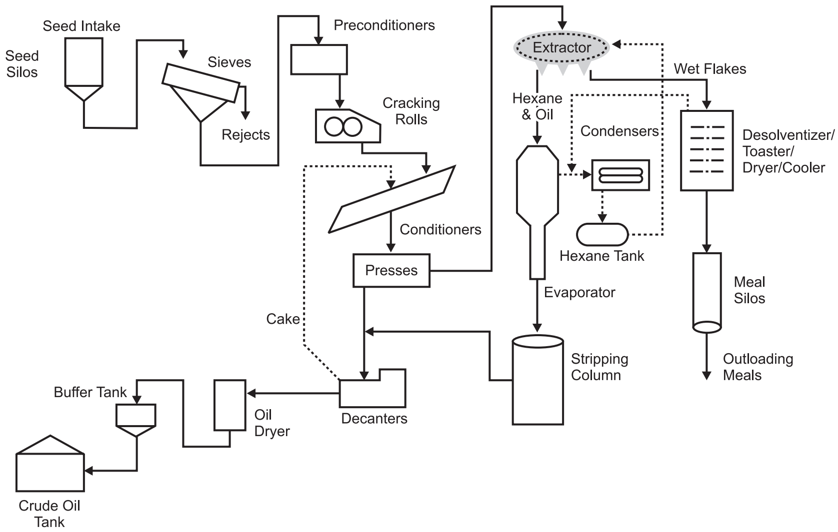


FIGURE 40.11 Oil processing.

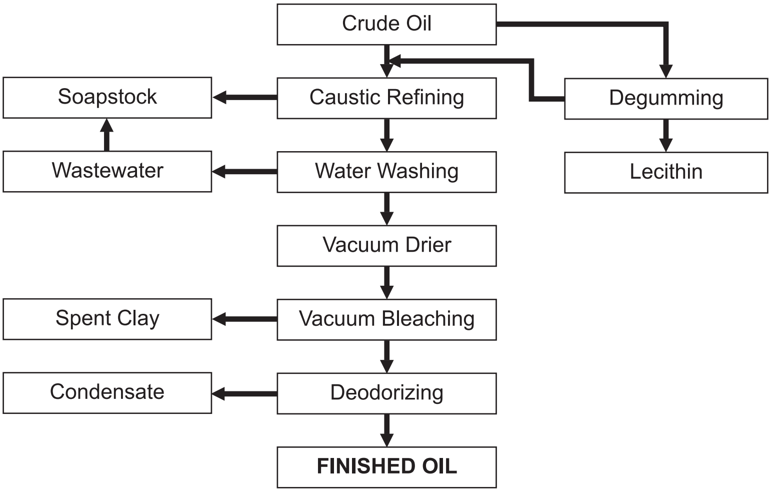


Figure 40.12 Oil refining process.

The oil refining process is shown in Fig. 40.12. Water degumming removes the gums or lecithin (phosphatides). This step prepares the oil for long-term storage or transport. Caustic refining removes the free fatty acids from the oil. Bleaching is performed using acid activated clays, like bentonite or montmorillonite. Bleaching improves the refined oil flavor and removes trace phosphatides, soaps, metals, and any color. Deodorizing removes additional free fatty acids and odoriferous compounds in the oil. This is accomplished through steam stripping. Therefore, good purity steam is necessary for the process to work efficiently.

Biofuels

The biofuels industry consists of fuel products created from renewable biological-based products. The two primary fuels are ethanol and biodiesel (fatty acid methyl ester or FAME). Water and energy use in these industries has increased substantially, due to the growth of the global demand for these products (Fig. 40.13). The following sections will focus on the dry grind corn ethanol process, as well as a general description of the biodiesel process.

Dry Grind Corn for Fuel Ethanol

The other predominant corn processing industry is the dry grind ethanol process (Fig. 40.14). The name, however, is misleading; there is a relatively high level of water used in the cooling of the process. It is only the first grinding step that is dry. Immediately, the ground corn falls into a slurry tank, where various recycled water streams are added, and the temperature is brought to 150 to 170°F (66–77°C). This

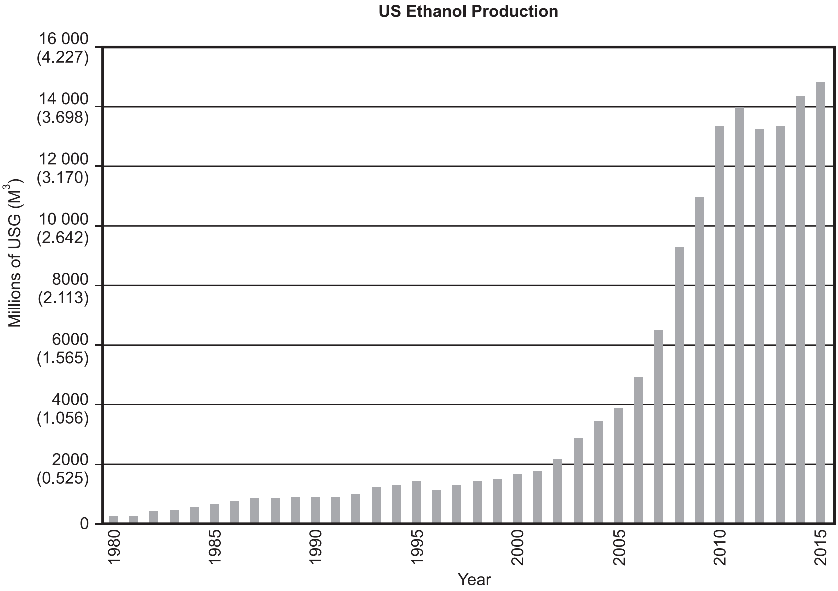


Figure 40.13 U.S. ethanol production. (*Adapted from information available from the Renewable Fuels Association www.ethanolrfa.org.*)

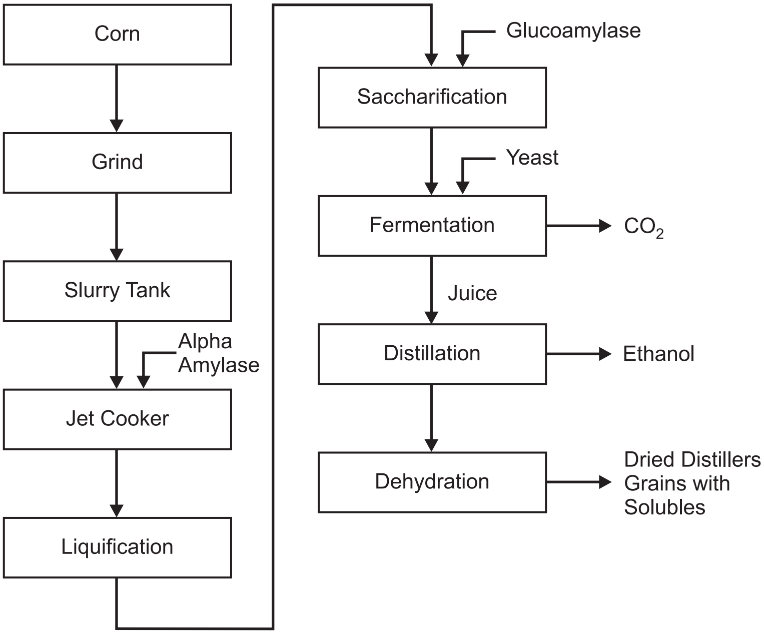


Figure 40.14 Dry grind ethanol process.

prepares the corn to enter the jet cooker, via either cook tube (direct steam) or shell tube cooker (indirect steam), depending on design. The corn mash slurry then enters the liquefaction tank, where alpha amylase enzyme is added to begin breaking the starch into polysaccharides in preparation for the next step of the process, saccharification. In most new facilities, saccharification and fermentation have been combined to increase efficiency. As glucoamylase is creating glucose, yeast is consuming it as food and producing ethanol.

After 50 to 60 hours, fermentation is complete, and the beer can be taken to distillation to remove ethanol. Distillation only achieves 95% ethanol, commonly referred to as 190 proof. In order to achieve 100% ethanol (200 proof), a drying process is required using molecular sieves. Through the molecular sieves, water is removed by passing the stream over a molecular sieve bed, where a water molecule is small enough to enter the sieve bead, but ethanol molecules are too large and pass by the bead, exiting the molecular sieve bottle as 200 proof ethanol (99–100% ethanol). The ethanol produced in the United States must then be denatured with natural gasoline (a by-product from the natural gas production process) to a 2 to 2.5% level. Then, a pH buffering/corrosion inhibitor product is added.

The "bottoms" of distillation or what is known as whole stillage (12–15% TS) is then sent to a centrifuge. The solids from the centrifuge result as wet cake, which is 30 to 35% total solids (TS) and either goes to a natural gas fired or steam tube dryer to form distillers dry grain (DDG) or can go directly to a feed pile for distillers wet grain (DWG). The liquid from the centrifuge (centrate) is called thin stillage (6–10% TS). Thin stillage has a portion (30–50%) sent back to the beginning of the process, and the remaining is sent to the multieffect evaporators to be concentrated to syrup that is blended with the cake.

This process is water and energy intensive. In 2016, water consumption is about 2.7 gallons of freshwater per gallon of ethanol produced (2.7 L/L). Electrical consumption is about 0.75 kWh/gal (0.20 kWh/L), and energy necessary is about 23 800 Btu/gal (6.63 MJ/L). These ratios are continually being reduced through new technology innovation created by the industry engineering firms and supplier partners. Water in particular has made significant progress, as ratios in 2003 were closer to 6:1. New technology is emerging to drive water use to a 1:1 ratio. As an example, all of the process water from most designs is zero liquid discharge (ZLD). Blowdown from the cooling tower is the only source of blowdown. Cooling tower evaporation can amount for 2.0 to 2.5 gallons of freshwater used per gallon of ethanol produced. Energy has been reduced through heat recycle. As an example, boilers producing steam are generally driven by exhaust from a thermal oxidizer. Boiler feedwater is generally pretreated by RO followed by a water softener. This is reverse from most industrial water processes configurations. It is done to reduce hardness loading on the water softeners in order to reduce the number of regenerations. This leads to far less backwash water and chlorides going to drain. Without a mechanical means for removal of hardness, antiscalants are fed to the front end of the RO units. In addition to the RO pretreatment, heavy focus is placed on additional utility water recycle.

Some biorefineries have been forced to ZLD. Once traditional methods of recycle are exhausted, many mills are forced to look to sophisticated capital solutions. In these designs, incoming plant water, generally from either a well or surface water, is treated by a series of RO units preceded with cold lime softening. These sophisticated pretreatment systems are followed by capital-intensive crystallizers to convert the final water flow to a solid. The ability to minimize this last remaining water flow has tremendous impact on lowering the capital costs of the ZLD systems.

Biodiesel

The biodiesel process (Fig. 40.15) is less complicated and uses less water and energy than the dry grind corn ethanol process. Biodiesel can begin with a variety of oil or fat-based feedstocks, including soybean, corn, corn distillers oil, canola, cottonseed, sunflower, beef tallow, pork lard, palm, or used cooking oil. Depending on the feedstock, the type of triglycerides varies greatly (Fig. 40.16). The type of triglycerides has a direct impact on the production of the end biodiesel and its attributes as a fuel.

The process of biodiesel production consists of transesterification, purification, alcohol recovery, and final fuel treatment. The feedstock oil is reacted with an alcohol, usually methanol (due to its lower costs), and sodium hydroxide. FAME, which is the biodiesel product, glycerin, and water are formed. The purification methods vary, but the purpose is to separate the three products as efficiently as possible. The separation process rate can be increased by the addition of settling aids. The glycerin by-product is used in many industrial and consumer products.

The resulting fuel is blended with regular petroleum diesel at various percentages. The final fuel product is referred to as “BX,” with the X representing the percentage of biodiesel in the product. For example, B5 is 5% biodiesel and 95% petroleum diesel. As the percentage of biodiesel increases in the fuel blends, undesirable properties begin to emerge. The properties causing most concern are poor cold flow and stability in the presence of oxygen. Which problem occurs is directly related to the type of triglycerides in the feedstock of the biodiesel. Fuels with a higher amount of saturated triglycerides will be very stable in the presence of oxygen but have poor flow properties in cold temperatures. When higher amounts of unsaturated triglycerides are found, oxygen stability is the predominant issue. To reduce the effects of these problems, fuel additives are added to the end product.

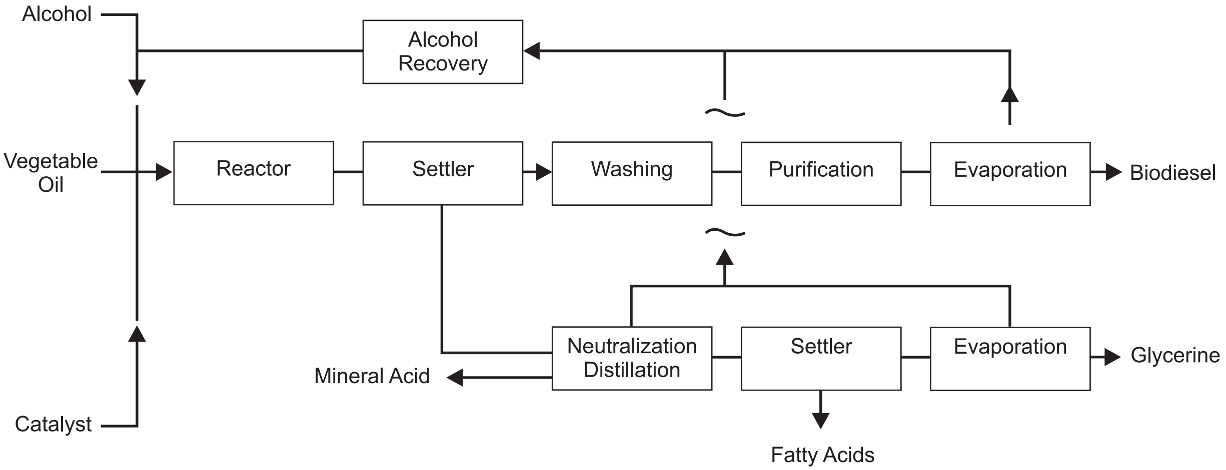


FIGURE 40.15 Biodiesel manufacturing process.

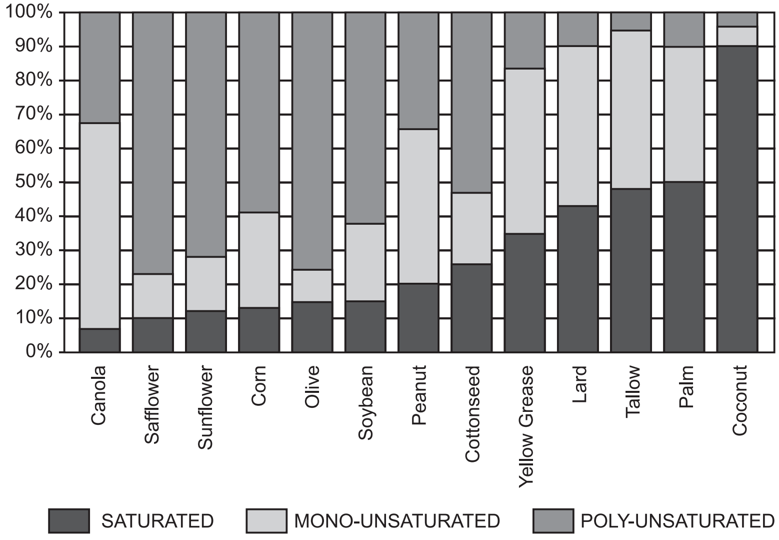


FIGURE 40.16 Triglyceride variance with biodiesel feedstock source.

Ethanol from Cellulose

The production of ethanol through the conversion of cellulose is the next major technological breakthrough for the biofuels industry. Major benefits are anticipated with this platform from increased greenhouse gas benefits to significantly higher energy ratios then corn to ethanol, or even sugar cane to ethanol.

Many different processes fall under the term cellulosic ethanol. In general, cellulosic ethanol is the process by which cellulose is extracted from feedstocks like energy crops (switch grass), agricultural residuals (corn cob and stover), or forestry products (hard and soft woods), converted to sugar by enzymes, and fermented to produce ethanol. Extraction will occur in an acidic or basic environment at high temperatures and pressures. This exposes the lignins, hemicellulose, and cellulose to be broken down into xylose and glucose through the application of cellulase enzymes. These sugars then pass into fermentation for ethanol production. The remainder of the process matches that of the corn or sugar ethanol production process. However, the residuals from distillation have no animal feed value.

The production scale use of energy and water to drive these processes is not well understood at the time of printing. However, looking to the corn process as a proxy, wastewater issues will substantially increase. This is due to distillation bottoms not having value as animal feed products as mentioned earlier. Without a higher value, it does not make it economically feasible to dry these products via expensive steam or natural gas. However, opportunity may lie in using them to fuel the boilers. Substantial research is going into how steam and power requirements can come from burning these solid wastes. In addition to the water and energy, several other key issues remain to be solved before economically feasible commercial scale plants will be constructed.

The Dairy Industry

The dairy industry is an important part of the food industry as a whole due to milk being a single source of the primary dietary elements needed for maintenance of proper health, especially in children and older demographics. The dairy industry is highly regulated due to the fact that milk could be a vehicle for disease transmission and has, in the past, been associated with disease outbreaks of major consequence.

Milk can come from a large variation in animals but for the purposes of this writing we will concentrate on cow's milk. Milk processing is similar for the other types of milk.

The use of water in processing dairy products is very important as it is used for heating, cooling, and cleaning. The effluent water from dairies also has to be treated, either onsite, or at a publicly owned municipal waste treatment facility.

This industry segment consists of fluid milk, cheese, and specialty dairy products. Each will be discussed separately. In addition, there are two important sources of water in the dairy industry that are highly regulated and will be discussed below. These are sweetwater and COW water.

Fluid Milk

Milk that comes directly from the cow, with no further processing is called raw milk and this is the main raw material for the dairy industry, including the fluid milk industry. The raw milk is transported to the dairy by tanker truck. The raw milk needs to be cooled either at the farm or upon transfer from the tanker to the storage silo at the dairy. The temperature for raw milk storage is less than 42°F (5°C). The stored raw milk is typically mixed occasionally to minimize the separation of components such as butter fat. The mixing also helps maintain a constant temperature. Milk contains the following average composition: 87.6% water, 3.6% fat, 4.9% lactose, 3.2% protein (2.6% caseins, 0.6% whey protein), and 0.7% minerals.

The raw milk is processed (Fig. 40.17) to yield pasteurized, standardized fluid milk for distribution to retail outlets and eventual consumption by humans.

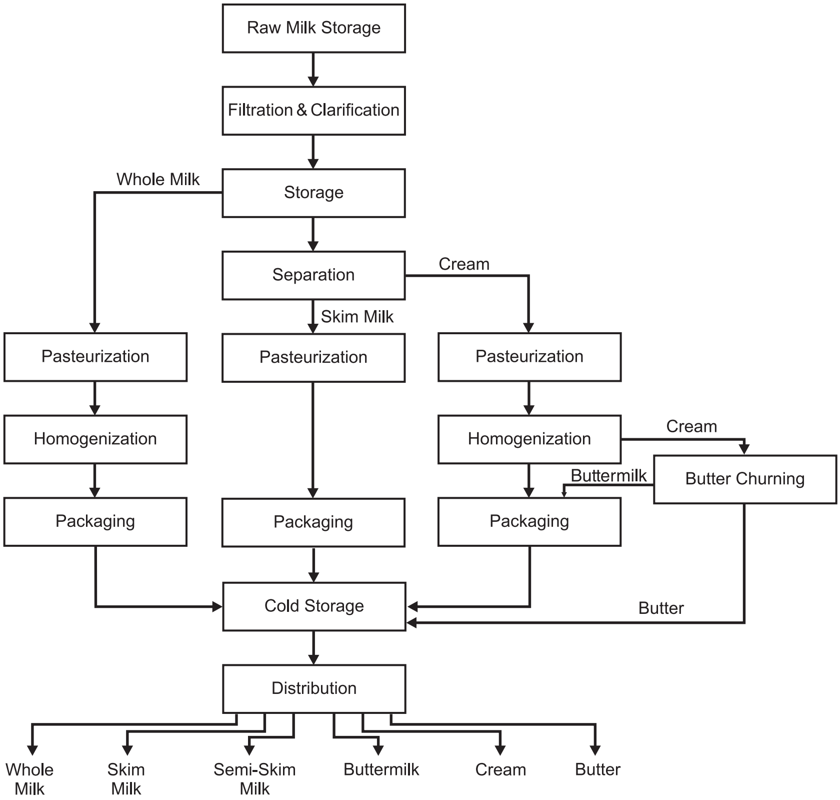


FIGURE 40.17 Typical fluid milk block diagram.

Water is used in several applications in a fluid milk dairy operation including:

- Cooling
    - Once through
    - Closed loop (sweetwater/ice builder)
    - Open recirculating
- Refrigeration
- Heating
    - Steam for hot water
    - Pasteurization
- Cleaning
    - Cleaning in place
    - Cleaning out of place

Cheese

Cheese originated in an effort to extend the shelf life of milk. Fluid milk is the ideal growth medium for microorganisms and is very susceptible to spoilage even when refrigerated. The goal of cheese making is to transform fluid milk into a relatively shelf stable, concentrated, highly nutritious and versatile form of food. The cheese making process includes the steps outlined below. One hundred pounds of milk produces ~9 to 14 pounds of cheese depending on the type.

- Coagulation of proteins
- pH lowering through lactic acid formation
- Removal of some calcium to alter the body and texture
- Lowering the water content through cutting, cooking, and agitating the curd and adding salt,
- And increasing the flavor through aging.

In cheese making dairies, milk is received, concentrated, standardized for fat and protein content, pasteurized, and put into a cheese vat. Cheese “starter” culture is then added to the milk and the milk is agitated. The cheese coagulates and is cut to form curds. The vat is then heated to “cook” the cheese. During this stage of the process, whey is separated from the cheese and is removed in liquid form for further processing, typically to make whey protein powder (Fig. 40.19). The curd is then pressed to form solid cheese which can be further aged or processed into shredded cheese, etc. The cheese making process can be in batches or continuous depending on the equipment employed. Figure 40.18 is the general flow of a dairy cheese plant.

Water is used in a cheese plant in similar ways; it is used in a fluid milk plant, for cooling, heating through steam, and cleaning. Cheese plants typically have a source of water from the concentrating of milk through evaporation referred to as COW water. COW water can be used in many ways throughout the facility if it meets certain standards set forth by the Grade “A” pasteurized milk ordinance (PMO).

Specialty Dairy—Concentrated Milk, Dry Milk, Yogurt, and Ice Cream

There is standard processing of raw milk that goes into specialty dairy products. These are the separation of the milk from the butter fat, obtaining the correct fat and protein mix and the elimination of pathogens. These steps are typically referred separation, standardization and pasteurization and are all fixtures of these different plants.

Concentrated milk is made by removing water from the milk to obtain a standardized solid content. The removed water is COW water can be reused elsewhere in the facility. Dry milk takes the

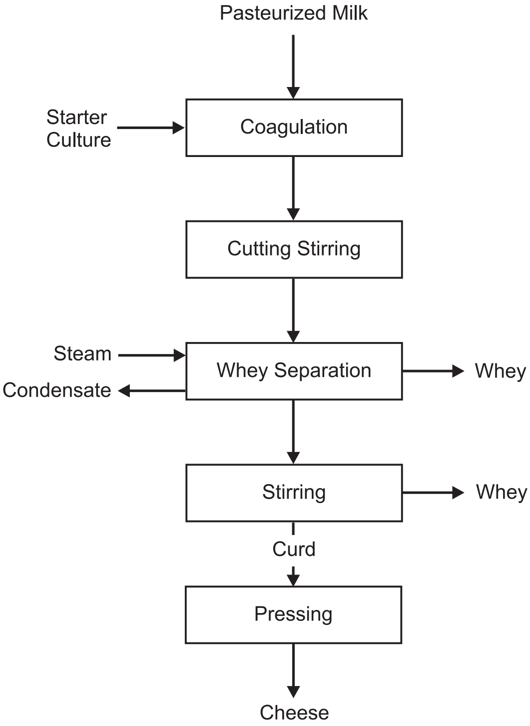


Figure 40.18 Dairy cheese plant block diagram.

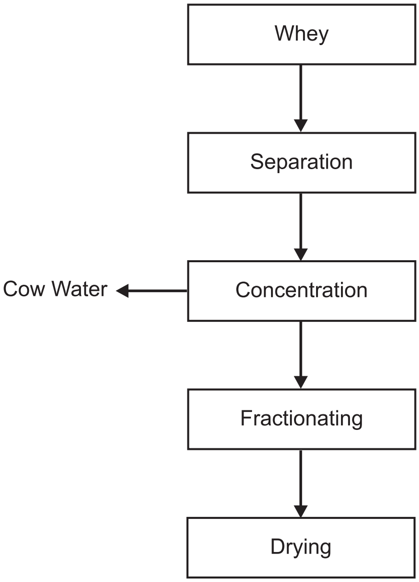


Figure 40.19 Flow diagram of whey processing.

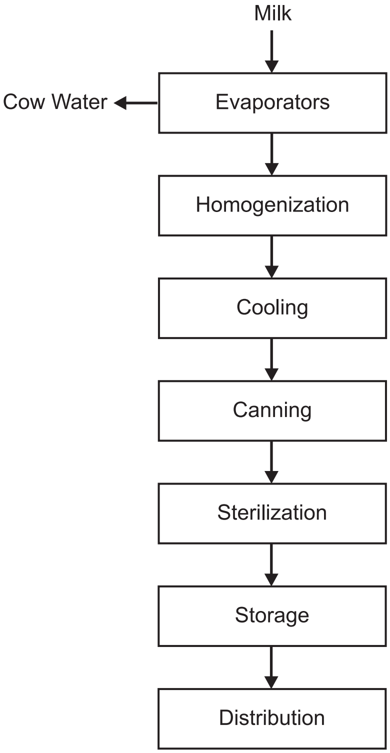


Figure 40.20 Typical condensed milk process diagram.

process further by removing a larger portion of the water to obtain a dry product that can be used as an ingredient or reconstituted with water to make milk. The making of dry milk allows milk to be shipped to areas that do not have milk production available locally (Fig. 40.20).

A dry milk plant typically uses evaporators to concentrate the milk. After the milk is concentrated, it is usually dried in a spray dryer (Fig. 40.21).

In a yogurt plant (Fig. 40.22), after pasteurization, separation, standardization, and homogenization, cultures are added to the milk, along with flavorings, to make the final yogurt process. During some of the yogurt making processes, whey is removed from the yogurt mixture which can then be processed by the waste treatment plant. In some, more modern plants, the whey is then stored and processed into whey powder.

In ice cream plants, several different options are available to obtain the correct mixture for the ice cream process. Some plants take in raw milk, pasteurize, separate, standardize, and homogenize to

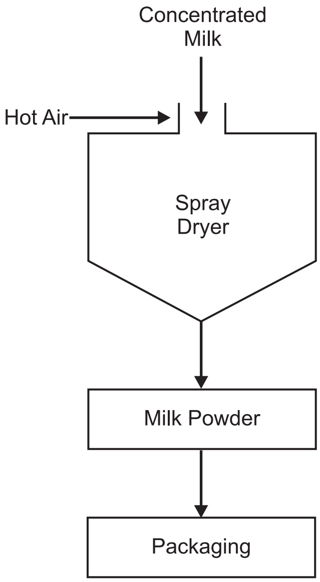


Figure 40.21 Typical spray dryer.

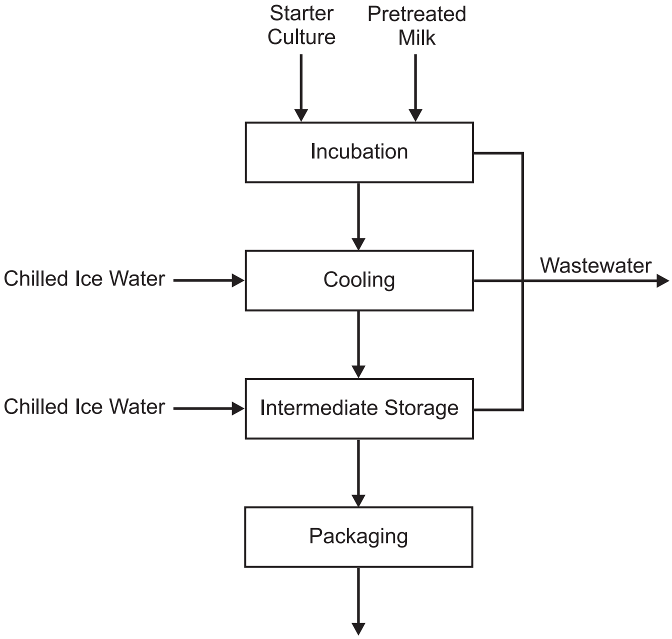


Figure 40.22 Yogurt plant block diagram.

obtain the correct fat content for the final product. In addition, ice cream plants can receive additional milk fat from other dairies as a raw material. In simplistic terms, the correct mixture, with flavorings and additives is then frozen and packaged for distribution. There are several different processes that lead to the final product including making bars, sandwiches, and other novelty items which increase the complexity of the plant.

Dairy Regulations

Dairy plants are some of the most regulated plants in the food industry. The most important document, regulating the dairy process in the United States is the Grade "A" PMO authored by the U.S. Department of Health and Human Services as a public health service as a portion of the U.S. FDA. This document portrays the regulations required from "farm to consumer." This is a comprehensive dictation of all regulations, including provisions for condensed and dry milk products and condensed and dry whey products. In an effort to keep up with additional regulations, this document is updated every two years. As of this writing, the most recent revision is the 2015 revision, which is available at the International Dairy Foods Association website, www.IDFA.org. The Grade "A" PMO includes regulations regarding water treatment, more specifically around the treatment of dairy sweetwater and dairy COW water which are both critical water applications in dairy plants.

Dairy Sweetwater

In milk processing plants, the pasteurization process is a basic operation and the pretreatment step when manufacturing all other dairy type products. The objective of the process is to eliminate pathogenic microorganisms; the plate heat exchanger is most commonly used for pasteurization where the milk is heated to 162°F (72°C) for at least 15 seconds, and then rapidly cooled by coolant of 36°F (2°C). For heating the milk, hot water at 165 to 167°F (74–75°C) is used. This water is heated by steam in a hot water heater. In the regenerative preheating section, the cold untreated milk is pumped into the pasteurizer where this cool incoming milk is preheated with the hot pasteurizer milk. This significantly reduces the temperature of the hot pasteurizer milk to 46 to 48°F (8–9°C). To reach a milk storage temperature of 39°F (4°C), the milk is further cooled by cold water, commonly known as sweetwater. The sweetwater loop is a closed loop as seen in Fig. 40.23.

The sweetwater closed loop varies in system volume, based on the size of the dairy plant, can be constructed of multiple metallurgies, is filled with potable water, and has engineering controls that ensure the pressure on the milk side of the exchanger is higher than the sweetwater to avoid contamination of the milk with sweetwater.

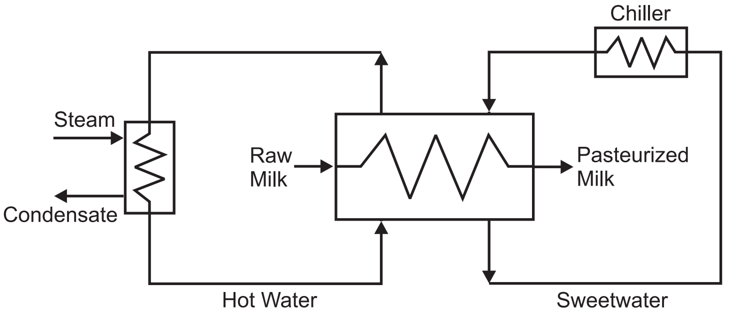


Figure 40.23 Typical Sweetwater system.

Like all closed loop cooling systems, sweetwater systems need to be treated to minimize corrosion and microbiological activity. Left untreated, they will foul and corrode leading to poor heat transfer. Corrosion and fouling negatively impact both production as well as food safety, and can lead to premature equipment failure and unscheduled shutdowns. The chemicals used for corrosion and microbial protection are mandated by the Grade "A" PMO.

Dairy COW Water

In milk processing plants, a large volume of water is generated when the milk is evaporated or concentrated up using either multieffect evaporator or process RO. Since the source of this water is from the milk, it is commonly called COW water. Within milk processing plants, this COW water can be recycled or reused, reducing the demand for freshwater. The dairy industry uses the Grade "A" PMO as a guideline to determine how to recycle or reuse COW water. The PMO has three categories, each of which is dependent on the end use application within a milk processing plant. The three categories are:

1. Category 1—Used for potable water purposes
2. Category 2—Used for limited purposes (such as boiler feed-water used for culinary steam or CIP prerinsing or cleaning solution makeup water)
3. Category 3—Used for other applications not referenced in the first two categories (such as boiler feedwater not used to production of culinary steam or noncontact cooling water applications)—In this category, the recycled COW water cannot be used in any circumstance where there is potential for incidental contact with milk or milk products

In a dairy plant where COW water is available, this is the single most valuable resource to reduce the use of freshwater in the dairy plant.

Foam Control

Within the food industry, there are many key application points in a variety of food processes where foam is inherently generated. The market segments where foam needs to be effectively controlled via an antifoam program include:

- Vegetable processing
- Ready to eat foods
- Snack foods
- Egg processing
- Potato processing
- Corn wet milling
- Edible oils
- Rendering
- Poultry washing
- Seafood processing

An effective antifoam program allows customers to maintain production throughput and the quality of the end product. With proper control, an antifoam program will help the customer's maintenance budget.

There are many types of antifoams available in the marketplace today. Whether they are silicone-based, water-based, or oil-based products, it is vital in these market segments to ensure the products have the appropriate food approvals.

CHAPTER 41

The Microelectronics Industry

The Microelectronic industry is a subsegment of the electronics industry, and includes, but is not limited to solar cell [photovoltaic (PV)], flat panel display (FPD), disk drive, silicon wafer, and semiconductor manufacturing. These industries are grouped together from a water treatment perspective for the following reasons:

- Similarity of manufacturing processes
- Similarity in use of water
- Similar water preparation processes
- Continued manufacturing innovation that warrants comments on water quality and use

The investment to build and equip a microelectronics fabrication facility (fab) is large; a large semiconductor fab could be a multibillion dollar project. Hence, the cost of production is high, and uptime is a key driver. It is important to remember that, just as there are different semiconductor end products [memory, analog, power, logic, micro-electro-mechanical systems (MEMS)], there are different manufacturing unit operation combinations.

Water is used in a wide number of applications in these industries. The following are some of the major applications, along with information on why the application is unique or critical.

Ultrapure Water

Ultrapure water (UPW) is usually considered the most critical water stream in the fab, since it directly contacts the product during the manufacturing process. A microelectronics fab uses UPW for a variety of reasons; to dilute process chemistry as it is applied, or to rinse

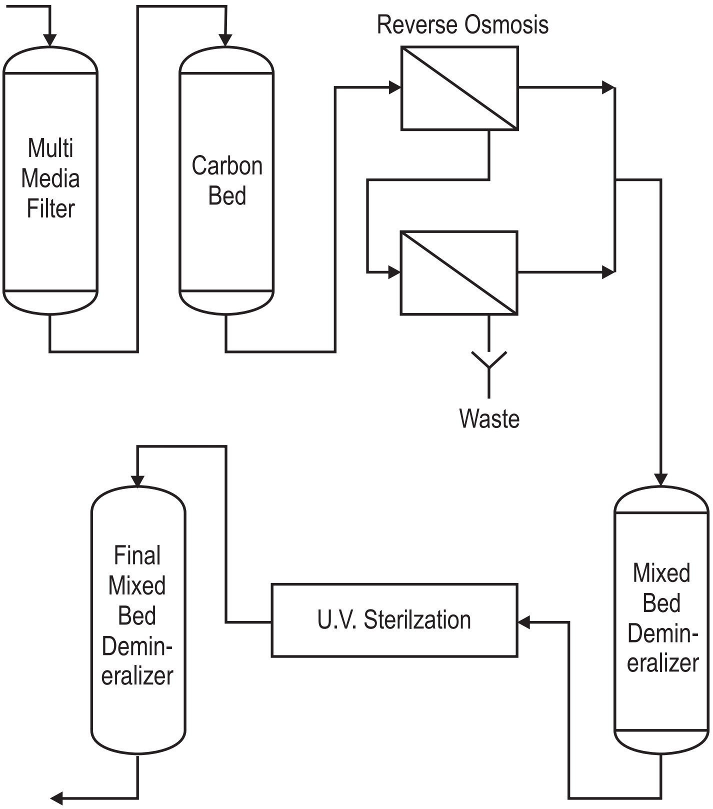


FIGURE 41.1 Typical UPW treatment operations.

process chemistry from the surface of the product during the manufacturing process. In either case, purity is critical. A UPW train may consist of the multiple unit processes (Fig. 41.1).

Due to the critical nature of this water stream, a sizeable investment is made in its monitoring and control; instrumentation for conductivity, pH, sodium, silica, resistivity, total organic carbon (TOC), and particle counting, are all common instrumentation features on a UPW system. It is also interesting to note that as the industry continues its microminiaturization trend, the demand for higher purity water increases correspondingly.

Typical challenges encountered in these systems include maintaining proper unit operations performance, coping with incoming water quality changes, achieving or exceeding asset life targets, keeping operational costs under control, and adapting to new water quality standards that are the result of an evolving manufacturing process.

In putting together a set of process units to meet high purity standards, the water chemist is faced with selecting equipment that reduces each of the following:

- Soluble matter—minerals, organics, and gases
- Particulate matter—filterable by a 0.22 μm membrane
- Colloidal matter—smaller than 0.22 μm, usually including silica and heavy metal oxides
- Biological matter—microbes, viruses, and metabolites

The unit operations available for meeting the goals of contaminant removal were presented in earlier chapters of this book. At this stage, it is important to recognize that selection of the best treatment processes requires knowledge of how each unit process relates to the others, as well as to the tasks each performs in contaminant reduction. For example, in some cases, a membrane unit [ultrafiltration, reverse osmosis (RO), or electrodialysis] may be best located ahead of an ion exchange unit, to reduce ion loading or to protect the resin from organic fouling. In other cases, the membrane unit may be best located after ion exchange, to eliminate organics that may be present as a result of deteriorating ion exchange resins, or to filter bacterial debris that may slough from the ion exchange beds.

Another factor to consider is the effect of flow rate on water quality. Two contributors to flow-affected quality are the ion exchange units, which should not be kept online at zero or low flows (less than about 20% of rated capacity), and the materials of construction of the storage and distribution system, which may contaminate water at low flow as a result of leaching organics from plastics or corrosion of metallic alloys.

The final UPW configuration depends on local water conditions and economics, growth potential for the fab, desired future flexibility, and other factors. Figure 41.2 illustrates how this process may come together at a plant. The function of each of the units shown on this flow sheet is described below.

Water clarifier—This is required if the water source is surface water containing suspended solids. Coagulants and flocculants may be applied to the clarifier for the removal of these solids, and chlorine may be applied for disinfection. If the water is hard (usually over 100 mg/L total hardness), the clarifier can be treated with lime for partial softening. The resulting high pH assists in the removal of heavy metals and in disinfection. If the raw water is taken from a municipal distribution system, the clarifier is unnecessary. An ion exchange softener may be utilized in this case to protect the downstream RO unit from fouling. The RO is generally controlled to produce a negative Langelier Saturation Index (LSI) in the reject stream.

Multimedia filter—This unit polishes the clarifier or lime softener effluent and reduces turbidity to below 0.1 NTU. It provides for the

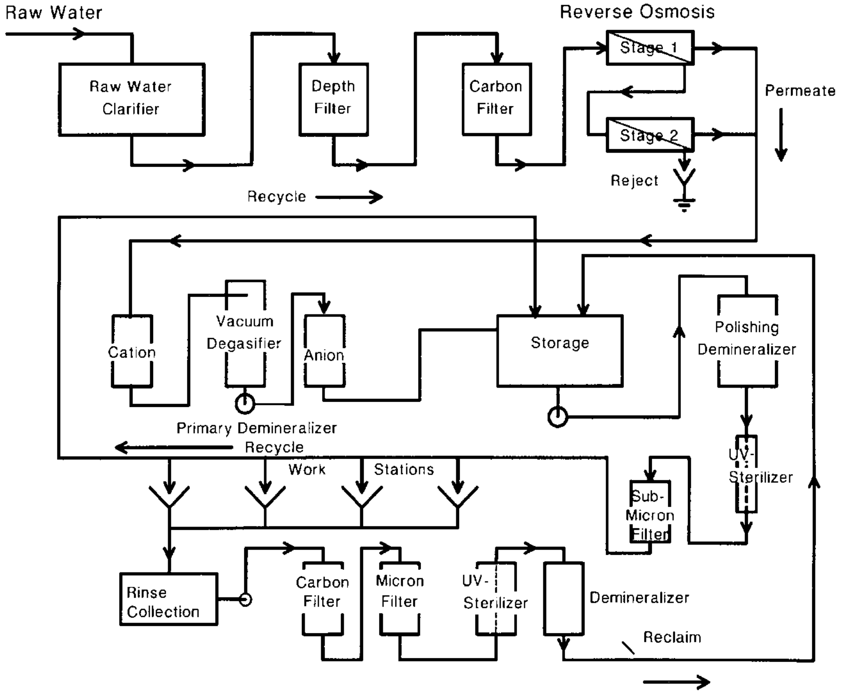


FIGURE 41.2 Schematic of UPW system producing rinse water for microprocessor manufacture. The rinse water after use is generally of such high purity that it can be reclaimed for other uses.

removal of many types of microbes; even viruses may be removed if consolidated into a filterable mass by flocculation. A filter is unnecessary if the first unit is an ion exchange softener.

Carbon filter—This filter serves two purposes: it eliminates residual chlorine by direct reduction and thus provides protection for the ion exchange resins downstream, and it adsorbs certain nonpolar organics from the raw water supply. This latter function helps to protect anion exchangers downstream from organic fouling.

Membrane separation—This process may include an RO unit that provides reduction in dissolved ions, reduction in dissolved organic matter, and filtration of colloidal matter, microbes, and microbial debris. The first benefit, reduction in dissolved ions, greatly reduces the ion loading on downstream ion exchange units. The second benefit, reduction in organics, improves the final quality and, at the same time, helps to protect the downstream ion exchangers from organic fouling. The third benefit, filtration of biological materials, protects the downstream equipment from either direct microbial attack or from becoming an incubator of microbial life; it also removes larger colloidal silica fractions. The RO unit may be replaced by a membrane ultrafilter (UF) that has all its advantages, except ion reduction, at a lower cost of operation and with lower loss of reject water.

Primary demineralizer—This is usually a two-bed ion exchanger, especially if the membrane unit contains RO membranes. However, this may be an evaporator, which provides for organic removal, disinfection, and degasification, operating effectively on an influent that has been processed by RO, while providing the additional benefit of reducing dissolved gases.

Storage tank—This unit is provided to allow for continuous recycle of downstream water to minimize leaching and degradation of water quality. A vapor space protection device, nitrogen blanketing, or both must be provided. They are, in fact, process units themselves, designed to protect water quality from degradation by airborne debris, especially microbes, as the storage tank breathes. Ultraviolet (UV) sterilizing lights may be mounted on this storage tank.

Polishing demineralizer—This is usually a mixed bed ion exchanger, but could be a RO unit, and electrode ionization (EDI), or an evaporator. In some plants, the polishing demineralizer is a nonregenerable unit with specially processed, nuclear grade ion exchange resins.

Ultraviolet sterilizer—UV irradiation using a wavelength of 254 nm provides for final nonchemical destruction of any microbes that entered the system after storage and survived the earlier treatment stages. The persistence of microbial contamination through successive physical barriers is an accepted fact to designers and operators of UPW systems. Conventional chemical biocides (e.g., chlorine) are to be avoided, because they represent a source of contamination. UV radiation oxidizes organic matter to produce carbon dioxide, which reduces resistivity. The sterilizer cannot always be used in this location, if the water contains excessive organic contamination at this point.

Submicron filter—This filter removes the residual debris, such as fragments of microbial cells, before the point of final use.

Point of use—There are often disposable mixed bed demineralizer cartridges containing special nuclear grade resin followed by submicron filters at each workstation at the final point of use. Since the excess water used in the rinse operation is often quite pure, it is reclaimed, reprocessed, and returned to the main storage tank. A special UV unit may be installed here for oxidation of organic matter at a wavelength of 185 nm.

Process Cooling Water

Process cooling water (PCW) refers to the loop of chilled water that is circulated to the tools (machines that perform discrete steps in the manufacturing processes). It is important to note that not all tools are water-cooled; some tools simply dissipate heat into the manufacturing area of the fab, where it is absorbed by the fab's chilled water loop. For those tools that are water-cooled, the PCW loop helps regulate the temperature of that specific manufacturing step, usually by providing dedicated heat removal. PCW loops may be primary or secondary chilled water loops off the main chilled water system.

The number of tools in a fab can be as high as several hundred. These tools represent the bulk of the investment in building a microelectronics fab. The cost of a single tool could be millions of dollars, depending on the manufacturing technology. Likewise, the cost of production is high, and production uptime is critical. In order for a microelectronics fab to remain commercially viable, it may upgrade its manufacturing technology by changing a set of tools. This change often involves disconnection and reconnection to process gases and fluids, process drains, and may involve the PCW loop. A successive tool may connect to the PCW loop, where its predecessor did not.

Despite the PCW loop's importance, it is often one of the most ignored water streams in the fab. A multitude of metallurgies can be present. These metallurgies are ever changing, as tools are added and removed as the fab upgrades.

Typical challenges encountered in these systems include proactive measurement of system performance and keeping track of system changes.

Cooling Towers and Chillers

The cooling towers in a microelectronics fab are used to cool the chillers, which in turn cool the PCW loops. As with PCW systems, reliability is critical.

The primary issues of corrosion, scale, and microbial fouling have already been covered within this book. Of specific relevance to the microelectronics industry is opportunities and pitfalls regarding water reuse to the cooling tower. The large quantities of water generated by the RO reject system in the UPW train, as well as the various process rinse waters, can be highly attractive opportunities for water reclamation and fresh water reduction. However, as with many opportunities, there are good ways and not-so-good ways of approaching them. Balancing water chemistries, local water and sewer costs, seasonal and process variability and quality, and effective monitoring and control technologies, are just some of the factors to incorporate into a site-appropriate strategy to minimize risk and maximize water reuse. Any water reclamation program involving the cooling tower must keep the heating, ventilation, and air conditioning (HVAC) asset, and the production it supports, at the forefront of its priorities.

Challenges associated with these systems include classic problems of scale, corrosion, and microbial control, with special considerations for water quality variations corresponding to the degree of water reclamation.

Wet Scrubber Systems

Wet scrubbers are used to improve air quality leaving the fab. They accomplish cleaning by mass transfer between the air stream to be cleaned (scrubbed) and a water stream passing through a packed column. These streams are oriented for cross- or countercurrent flow of the air and water streams. Typical contaminants to be removed include ammonia; sulfuric, phosphoric, nitric, hydrofluoric and hydrochloric acid fumes; and various organic solvents.

Normally, wet scrubbers are designed to prevent corrosion; metals are rarely used. However, scale and microbial growth can occur.

Challenges associated with these systems include understanding the nature and composition of the streams being scrubbed, having good analytical data on the chemistry of the water being used in the scrubber, and understanding the variability (quality and quantity) of both air and water streams.

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CHAPTER 42

The Building Materials Industry

We see them every day, but seldom do we take the time to really think about where they come from or how they are made, until we decide to fix our leaking roof or renovate our kitchen or bath or, better yet, build a whole new house. We are talking about building materials, those essential components that allow us to build our homes and businesses to be comfortable and effective in what we do on a daily basis.

As our population grows and our societies become more complex, we have a larger need for more and different types of building materials. That need has led to a reduction in our natural resources that in turn has resulted in the development of newer technologies for building. Many different materials are used for residential and commercial buildings. Two of the more common technologies are fiber cement and fiberglass mat. Both of these materials are relatively new on the scale of products used for building in comparison to wood, brick, or metal; however, they have been around for more than 40 years. Fiber cement and fiberglass mat have become fully integrated into our building processes and are used in many different applications in both residential and commercial building.

Fiber Cement

Fiber cement is a process that utilizes pulp, cement, silica, and sand to make durable building materials such as siding products, backerboard, and pipe.

Fiber cement siding provides low maintenance and does not sacrifice the beauty and character of wood. It resists rotting, cracking, and damage from rain and hail. It is noncombustible, with an expected use life of up to 50 years. This siding is available prefinished and may have a 15-year paint warranty.

Fiber cement backerboard, used in potentially moist areas like kitchens and baths, is a moisture and mold resistant substitute for drywall or a backerboard for tile applications. Cement board is a common solution for wet area floors, walls, ceilings, and countertops. Although no system is mold proof, this product delivers the ultimate in mold resistance, passing industry mold tests.

Fiber cement pipes are the product of choice for many below ground storm water drainage applications, providing significant installation and performance benefits over traditional reinforced concrete or steel. The expected service life of over 100 years, the comparative lightweight composition, the construction load capacity, and the availability of longer standard pipe lengths, makes these pipes a product of choice in many applications.

There are two distinct manufacturing methods for fiber cement—Hatschek and Fourdrinier. Each requires different process chemistries to operate effectively (see Fig. 42.1 for a general process overview).

Water is used throughout these processes. Water is the primary solvent used to disperse and carry the pulp, cement, sand, silica, and chemistries that actually make up the finished fiber cement product. This water is drained, collected, and recycled as part of the normal

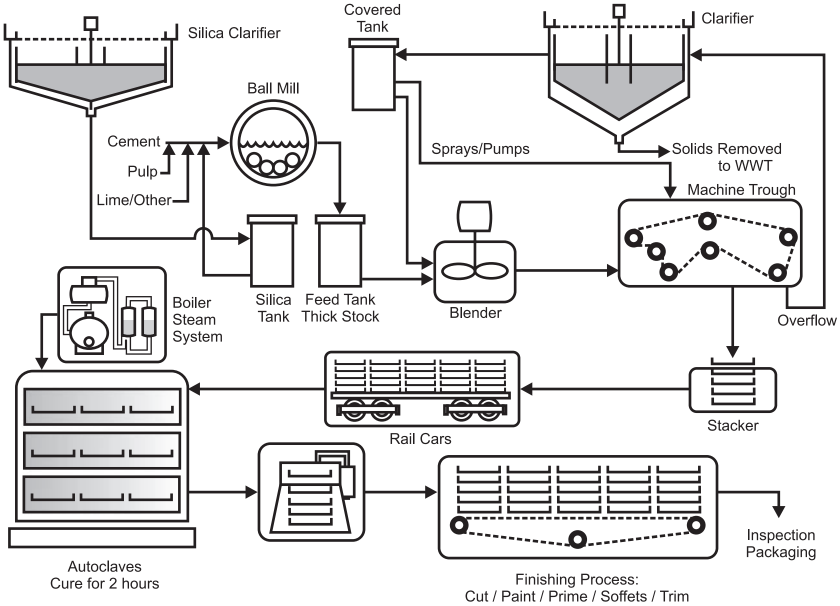

FIGURE 42.1 Fiber cement process overview.

operating process. Chemicals are used throughout this process to enhance product quality, production speed, etc.

Water is also used in the steam boiler operations in these plants. Steam is often used in autoclaves to cure the fiber cement product before further processing to finished goods. These autoclaves are typically operated at 170 psig (1.2 MPag), and product is cured for approximately two hours. In addition to use in the autoclaves, steam may also be used for plant or office heat.

The typical steam boiler plant design will consist of makeup water from the local municipality or local ground or surface water, treated by sodium softeners to remove hardness. This water will then be deaerated to reduce dissolved oxygen. The feedwater will then go to two 200 to 250 psig (1.4–1.7 MPag) boilers of either watertube or firetube design. Steam from these boilers will primarily supply the autoclaves, where it will condense and be collected in a condensate storage tank. This condensate will often be pumped through a plate-and-frame makeup water preheater before sewer discharge. These plants do not typically return condensate to the boilers, as it is most often highly contaminated with by-products from the cured fiber cement.

Problems associated with these boiler water applications are not unlike traditional difficulties experienced in other low-pressure boiler operations. The makeup water must be softened to less than 1 mg/L total hardness to avoid scaling of boiler internals. Because these boiler systems are typically 100% makeup with no condensate return, this is a very critical step. It is common to see poor quality makeup water due to improperly operating softeners. These units should be audited regularly to insure effective operation.

The makeup water must be deaerated to less than 7 μg/L dissolved oxygen to help prevent feedwater and internal boiler corrosion. Typically, a catalyzed sodium bisulfite is added to the deaerator storage to further reduce dissolved oxygen to below critical levels.

To help prevent deposition in the boiler internals, an internal boiler chemical treatment program should be utilized. Any conventional low-pressure boiler program can be used. Regardless of the chosen chemistry, the goal is to prevent deposition of hardness and iron in the boiler while reducing corrosion rates.

A final area of concern in these boiler systems is the makeup preheat exchanger. The condensate from the autoclaves is often pumped through an exchanger to preheat the makeup water thus reducing plant energy consumption. This condensate often contains significant contamination from the fiber cement in the autoclaves. This contamination may cause fouling or scaling on the condensate side of the heat exchanger, leading to reduced heat exchange or even plug gage. To prevent this, a high-temperature polymeric dispersant is often employed. Typically, corrosion is not a problem on these exchangers due to the use of corrosion-resistant construction materials.

Fiberglass Mat

Fiberglass mat refers to a material that is typically used in the roofing industry to make various forms of shingles and roofing barriers. It is also starting to be used as a replacement for paper in the production of drywall sheeting. As one might expect, fiberglass mat is very tightly tied to the building materials market place and specifically the roofing industry. It is made through either a wet-lay or dry-lay nonwoven process that produces a base sheet called mat. In the wet-lay process, the mat is produced using fiberglass chop, binders, dispersants, and surfactant. Mat must meet physical specifications for tensile strength, dispersion, and tear strength.

In the wet-lay process, chemically sized chopped glass fibers of the type, diameter, and length suited to the customer's application are slurried in water and then spread uniformly across a fine mesh belt. This thin layer is impregnated with an appropriate resin binder, dried, cured, and finally wound into rolls. This wet-lay process produces economies of scale, because of its relatively high throughput when compared to dry-lay mat manufacturing processes. It also offers a more consistent and uniform mat than other forming techniques.

Roofing products strengthened with a glass fiber substrate keep their shape during shipping and handling. Once installed, the reinforced shingle provides superior strength and dimensional stability over a wide range of temperatures, without absorbing moisture as organic felt shingles do.

Because it is inorganic, the glass substrate has excellent resistance to rotting and mildew. As a result, the shingle performs better and longer than those made with alternative substrates. They also require less sectant asphalt than organic shingles, as glass mat is an ideal porous reinforcing media.

The major raw materials consist of, glass fiber, sizing, water, resin binders, adhesive enhancers, and specialty chemicals for white water preparation.

The wet-lay process tends to flow as discussed below and shown in Fig. 42.2.

The major components of a typical fiberglass mat machine are:

- Head box
- Forming wire
- Vacuum forming box
- Broke chest
- Machine silo or DELTAFORMER™
- Collection chest
- Clarified chest
- Water storage chest

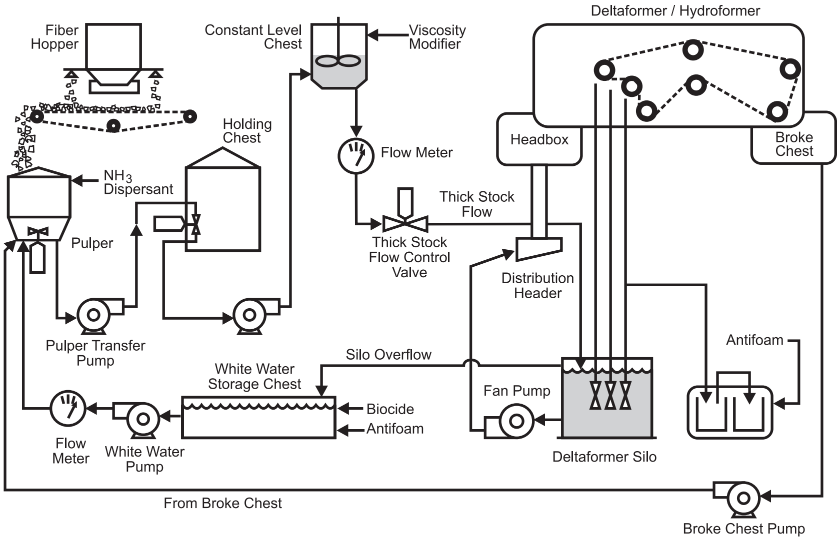

FIGURE 42.2 Fiberglass mat manufacturing.

The fiber feed system automatically feeds a specified quantity of fibers to the pulper that blends the fibers, water, and chemicals with agitation to disperse bundles of fibers into filaments in the thickstock slurry. The machine/holding chest acts as a surge tank and buffer between the batches from the pulper and allows for continuous thickstock flow. The constant level chest provides a constant head to the flow control valve to give a steady flow through the valve and pipe.

Head box—The head box is a large flow control chamber that feeds the stock to the forming wire. Sufficient agitation is maintained by means of baffles. This agitation ensures the proper mixture to prevent flocculation of the fibers. The agitation spreads the fiber slurry evenly to the full width of the wet-lay machine to provide delivery of stock to the forming wire.

Forming wire—The forming wire is a polyester fabric of various weave patterns used for fiber deposition and to carry formed fiberglass mat. The goal is to form a continuous and uniform web of fibers. To accomplish this, the white water slurry is controlled to lay fiber out on the former wire.

Vacuum forming box—The vacuum-forming box removes excess water in the sheet before binder saturation. A binder solution is added to the fiber web to essentially "glue" the fibers together. After the binder is added, the water is removed via vacuum, and the sheet is sent through a drying and curing process to complete the chemical reactions to bond the fibers.

Broke chest—The broke chest collects the wet trim, full-sheet dumps, water, and fibers from the wire until they can be pumped back to the front of the process.

Machine silo or DELTAFORMER™—The machine silo returns white water from the formation zone, deaerates the water to reduce foam, and supplies a constant head of water to the fan pump.

Collection chest—The collection chest collects white water from the vacuum separators and the white water silo to be used to supply the filter system.

Clarified chest—The clarified chest holds water returned from the filter screen until it is pumped to the high-pressure showers.

Water storage chest—The water storage chest water is sent to the pulper to make up white water batches.

Water is a key element in the production of wet-lay fiberglass mat. Water is the primary carrier of the fibers that make up the mat. Mat thickstock, as it is called, is a combination of water with chopped up and sized glass fibers and proprietary specialty chemicals, including viscosity modifiers, dispersants, antifoams, and biocides. This mixture is often referred to as white water due the white color of the slurry. The quality of water, including its pH, temperature, and total hardness, is critical in attaining the expected product results. Through monitoring and controlling these variables and the applied chemistries, the fiberglass mat manufacturer can modify the type, quality, and speed of production.

CHAPTER 43

The Automotive Industry

The automotive industry segment is composed of a variety of automotive manufacturing operations, including parts manufacturing, body manufacturing, and vehicle assembly. Within these different manufacturing processes, four basic operations are found in the production of most of these products:

1. Casting (foundry operation)
2. Machining
3. Stamping and fabricating
4. Final assembly

Some plants may perform just one of the above operations, while others carry out the entire process from casting through assembly at a single integrated plant. Figure 43.1 shows the flow of material for the total operation of an automotive plant. Although water consumption is relatively modest in each of these operations, water quality is important, and aqueous wastes are quite concentrated.

Foundry Operations

In the foundry, parts such as crankshafts, engine blocks, and transmissions are cast. In a typical iron foundry, pig iron is purchased from a steel mill and melted in a furnace called a cupola, similar in design to a blast furnace. The iron is mixed in the furnace with a charge of coke and a flux or slag-forming material, which may be limestone or fluorspar. Air is blown into the furnace at the tuyeres, as in the blast furnace, and the combustion of the coke melts the charge, with molten iron draining to the bottom and slag floating to the top.

The gases leaving the cupola are combustion products, predominantly carbon dioxide (CO_2) with perhaps a small amount of carbon monoxide (CO) plus a small amount of sulfur dioxide (SO_2), if the coke was made from sulfur-bearing coal. When the charge is

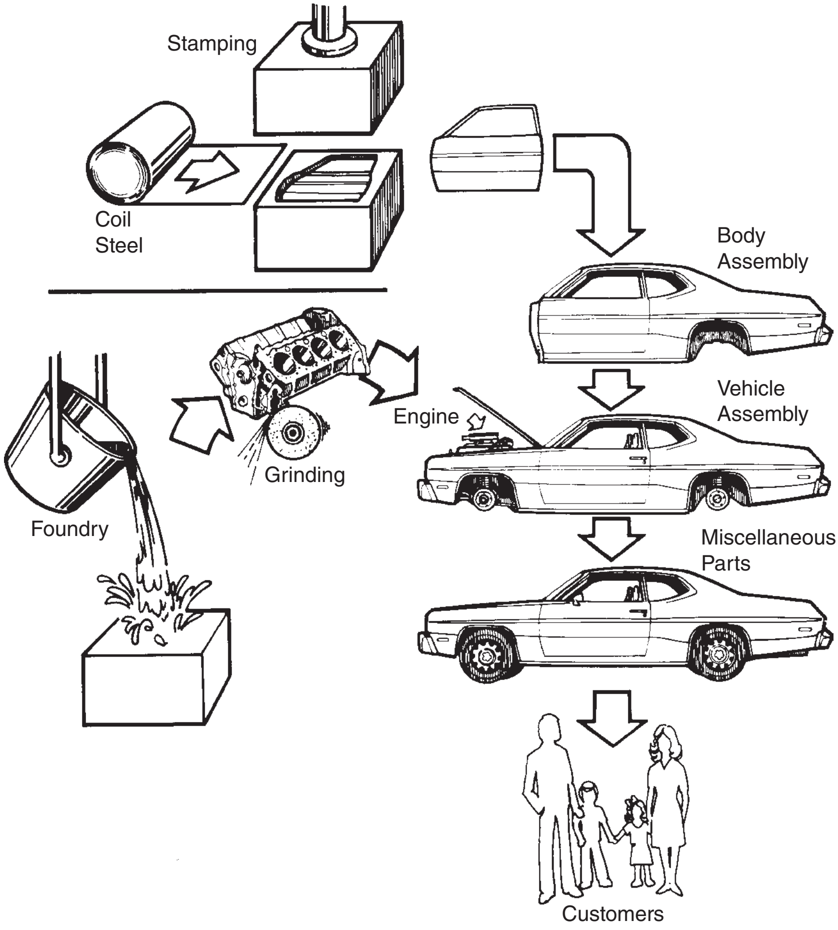

FIGURE 43.1 Basic automotive manufacturing.

dumped into the burden, there is some breakup of the relatively weaker coke lumps, and there is an initial surge of coke fines into the exit combustion gases. There usually is iron oxide broken loose from the bars of pig iron, so the discharge from the cupola is high in suspended solids (SS).

To avoid creating an air pollution problem, the foundry may install a baghouse for dry collection of the dust or a wet scrubber. If the latter is installed, this becomes the principal use of water in the foundry operation. A typical foundry operation is shown in Fig. 43.2.

Because the products of combustion are acidic, the pH of the scrubber water is generally quite low. Figure 43.3 shows a pH chart taken from a recorder sampling scrubber water. The effect of opening

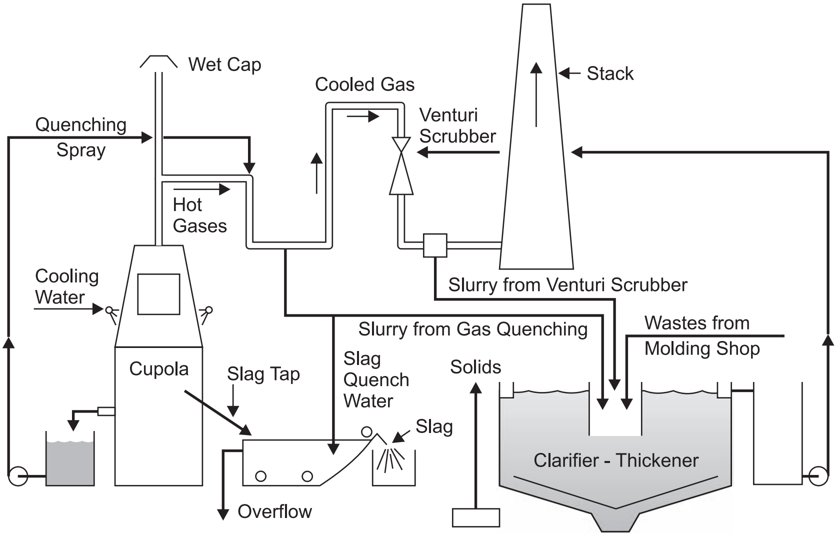

FIGURE 43.2 Water circuit in a gray iron foundry with wet scrubber.

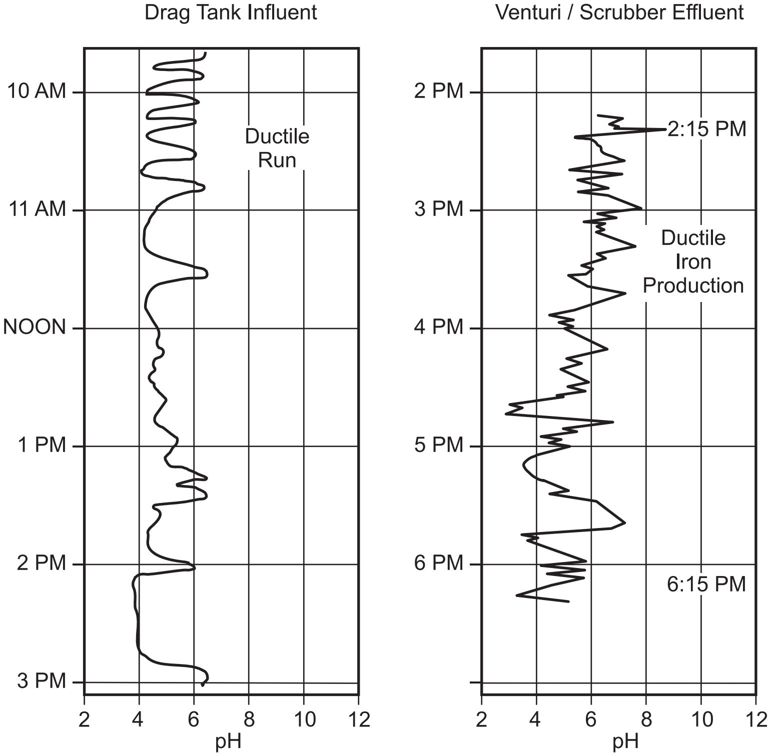

FIGURE 43.3 Strip charts showing pH variations in Venturi scrubber effluent.

and closing the charging door is to dilute the stack gases, which is apparent on the strip chart.

A second use of water in the foundry is for cooling the cupola shell. This is usually done by direct spraying of the steel shell with water through a circumferential pipe at the top of the cupola. This water may be collected at the bottom of the cupola, pumped over a cooling tower, and returned to the top of the cupola. Most foundries adjust pH and add a corrosion inhibitor to protect the cupola shell.

A third use for water is in the granulation of slag tapped from the cupola. The molten slag collects in the granulation tank, and the slag grains are removed by flights up a ramp and discarded into a tote box.

Most foundries encounter dust problems in the preparation of sand molds and the breakup of the sand from the finished casting, where the material is crushed for return to the molding room. A variety of chemicals may be mixed with the sand to produce the green mold, which must be cured before molten metal is poured into it. Phenolic compounds are sometimes used in preparing the mold, so phenol may be present in the foundry wastewater, both from this source and from the coke charged to the cupola. Oils may also be used in the preparation of the mold, and these volatilize during the baking of the mold and must be collected by a wet scrubber. Depending on the operations, there may be individual wet scrubbers at the cupola, the sand mold, and the shakeout room, or wastewater from these areas may be combined before treatment.

Table 43.1 shows the analysis of a foundry wastewater related to the installation illustrated in Fig. 43.2. The oil content was quite high, but there was no evidence of free oil in the sample. This is a common occurrence, where the bulk of SS consist of carbon and iron oxide, as in foundry operations.

After the treatment of this particular wastewater, the oil content was reduced to less than 50 mg/L, SS to about 56 mg/L, and phenol to 0.5 mg/L. The collected solids were vacuum filtered for disposal, and the oil content of the dry cake was about 15%.

Constituent	mg/L
TDS	770
SS	1900
Extractables (oils and grease)	290
Phenols*	1.5
pH	7.6

*Present in the coke and core binders

TABLE 43.1 Analysis of a Typical Foundry Wastewater

There is often some fluoride present in the wastewater, which may be introduced by volatilization into the cupola stack gas, or may be dissolved from the slag in the granulation tank. Since most foundries discharge into a city sewer, the amount of fluoride is not usually so high as to require special treatment.

There is evaporation of the scrubber water, leading to concentration, so that chemical treatment is usually required for control of scale and corrosion in the recirculating system, and special alloys are often required for the circuits of a multiple-circuit washer, where the pH may become very low.

Machining

Rough cast parts are sent to power train plants to be machined and assembled. Figure 43.4 shows the typical operations in a plant that machines parts for and assembles car engines. Major operations include machining, cleaning, engine testing (hydrotest), and waste treatment.

Rather than a single assembly line for the machining operation, a series of small lines is set up for each part and department. Each department performs its own particular machining operations on the subassemblies, and each of these may require a specific type of machine coolant, varying from water-based material to

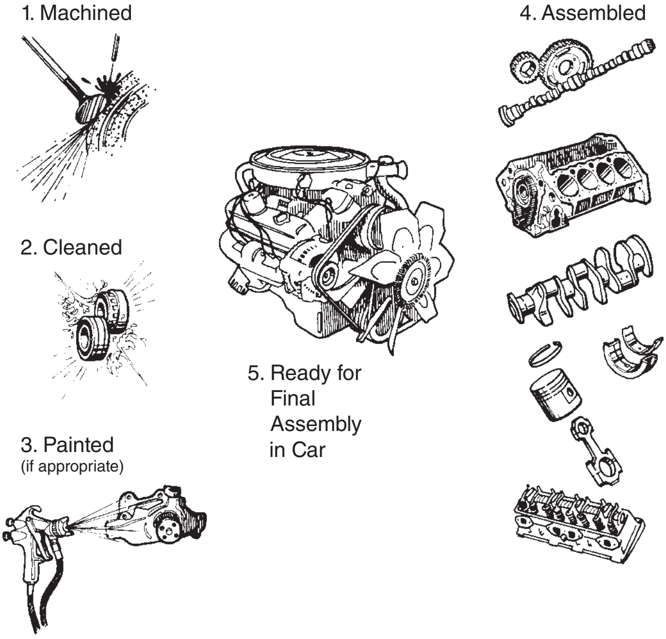

FIGURE 43.4 Typical operations in an engine plant.

heavy sulfur oil. These coolants provide lubricity and cooling to the metal and tool used for shaping. Many of these oils contain emulsifiers that readily create oil–water emulsions when mixed with water.

Some coolants are soluble synthetic and semi synthetic oils. The synthetic coolants contain no oil, while the semi synthetics contain some oil but less than soluble oil coolants. These have some advantages over soluble oils in the machining process.

Soluble oil coolants are usually maintained at 5 to 15% oil concentration and stored in central sumps. The oil is recirculated through screens or filters to the machine tool and back to the sump. At the machine, the soluble oil absorbs heat and picks up metal fines and hydraulic oil from leaks. Plants will normally dump part of the coolant system periodically, because the emulsion is no longer stable or the coolant is contaminated with bacterial growth. It is good practice to add biocide to control bacterial activity, but even this cannot extend coolant life indefinitely.

City water is used to make up the coolants. If high hardness levels are found in the makeup water, soft water is sometimes advantageous, because calcium ions tend to destabilize the emulsions, especially if the coolant concentrates. Removing the calcium and magnesium extends the stability of the soluble oils.

Parts Cleaning

Another major operation in the machinery plant is cleaning. The parts must be cleaned before and after machining to remove dirt, rust preventive, and coolant. Chemical cleaners are used, usually alkaline and nonionic surfactants. The cleaner usage is substantial, since the cleaners are continually depleted and fresh chemicals are needed to maintain the strength necessary for effective performance.

In the machine shop, blowdown from the parts cleaners may represent a significant portion of the flow to the waste treatment plant. Because a primary function of the cleaner is to remove coolant, blowdown usually contains high levels of oils and synthetic oils. These wastes are emulsions stabilized by the surfactants in the coolant and in the cleaners. Other flows to the waste plant include soluble oils, other cleaners such as floor cleaners, cooling water from a variety of sources (such as air conditioning systems), boiler blowdown, hydraulic oil leaks and spills, and other process waters.

Changing from soluble oil to synthetic coolant has caused problems in the waste treatment plant, when acid and alum were being used for emulsion breaking. Organic emulsion breakers have proved more effective in removing oil from the effluent under a wide variety of coolant selections. However, reduction in soluble biochemical oxygen demand (BOD) by alum or organic emulsion breakers is usually very limited. BOD loadings to the waste plant may actually increase, since synthetics usually have higher BOD than soluble oils.

Constituent	mg/L
Hexane extractables	4000
P alkalinity (as $CaCO_3$)	424
Total alkalinity (as $CaCO_3$)	708
SS	300
Total iron (as Fe)	4
TDS	1500
pH	10.4
Calcium hardness (as $CaCO_3$)	20
Total hardness (as $CaCO_3$)	26
Total phosphate (as PO_4)	3

Table 43.2 Raw Waste from Machining Operations

Another factor that can have an impact on the quality of the waste treatment plant effluent is process cleaner usage. Excessive cleaner usage, especially of certain strong nonionic cleaners, can increase dosages in the waste treatment plant or even make the waste virtually untreatable. The volume and type of cleaner should be balanced against the impact on both the cost and quality of the waste treatment plant operation.

Table 43.2 shows a typical analysis of untreated effluent from a machining plant. The effluent is an oil-in-water emulsion. This analysis does not include free or floating oils.

Utilities

Machining plants use cooling water for air conditioning, powerhouse diesel generators, air compressors, hydraulic oil coolers, and furnace cooling if the plant is involved in heat treatments such as annealing.

Each plant, depending on what it manufactures, may have its own unique uses for cooling water. For example, engine plants typically hydrotest the assembled engine on a dynamometer before shipment. A typical test system is shown in Fig. 43.5. On the tube side or closed side, the heat exchanger takes the place of a radiator. Soluble oil products are used on the closed side, if the engine is going to be drained before shipment. These products lay down a film that prevents flash corrosion. If the engine is not going to be drained, either soluble oil or conventional corrosion inhibitors can be used, depending on the manufacturer's restrictions.

A typical boiler plant generates steam primarily for heating various cleaner and bonderizing baths, but the winter heat load is also significant. Therefore, summer steam demand is light. If the plant has a forging operation, steam may be used to drive the hammers (Fig. 43.6). Sodium softening, reverse osmosis, and demineralization are the most common methods of pretreating boiler makeup water.

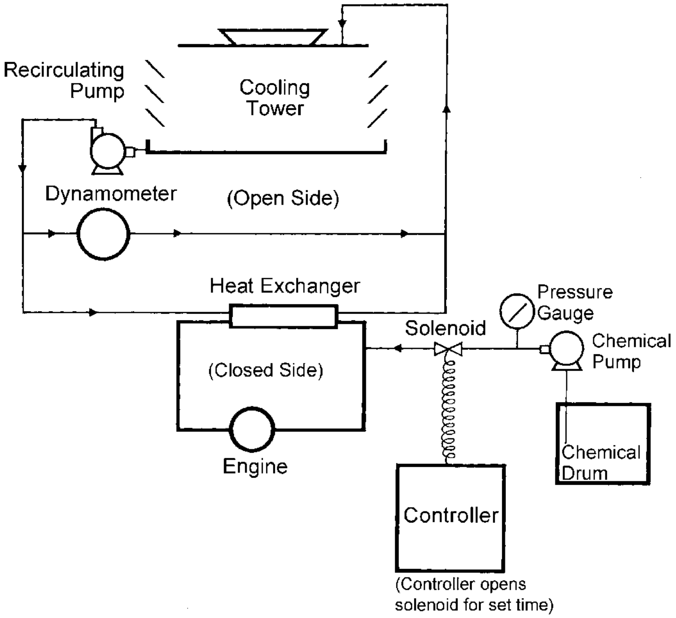

Figure 43.5 Cooling water circuit for hydrotesting finished engines.

Paint Spray Booths

Some machinery plants (such as engine plants) have small spray booths, where primer is sprayed on parts. These small booths experience the same maintenance problems as larger ones, such as those used to paint car bodies, and they require chemical treatment. They are not as important to production, so they are frequently poorly maintained.

Since spray booths are so widely used throughout the automotive and machinery industries, a description is given here to illustrate the type of water technology required for successful operation. Goals of the water treatment program are:

- Keep the water circuit free of deposits.
- Make the paint overspray collected in the water nonsticky and readily removable from the water.
- Minimize deposits to prevent obstructing flow of paint-laden air from the booth.
- Minimize contaminants in the air discharged to the outside so it will not create an air pollution problem.
- Minimize booth maintenance.

Figure 43.7 illustrates a typical paint spray unit for small parts, such as would be found in the machinery plants. The conveyor

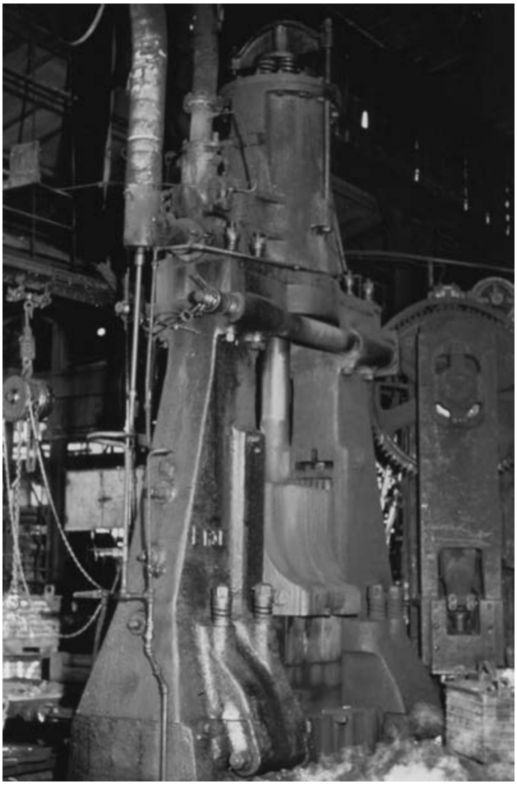

FIGURE 43.6 Large steam-operated forging hammer. The dies and sow block have been removed for routine maintenance. (*Courtesy of Forging Industry Association*.)

carrying the parts to be painted passes in front of the wet well, and the operator sprays paint on the parts as they pass by, with the excess or overspray being collected on the film of water flowing down the wet wall. The water must be chemically conditioned so that the pigment and the excess vehicle and solvent are killed and do not form a sticky mass that would be difficult to remove from the pan. Water is continually withdrawn and recirculated to the spray header, which provides scrubbing of the ventilating air discharge before water drains back down the wet wall.

The large paint spray booths used in the automobile assembly shops are illustrated in Figs. 43.8 and 43.9. Robots and operators work inside these booths, applying paint to the car body. The floor of these units is grating supported above a water basin, and falling paint deposits on the water, while other paint particles are carried by the air flow into the water curtain either on the wet walls or into the wall cavity, or back section, where additional sprays scrub the flow of air.

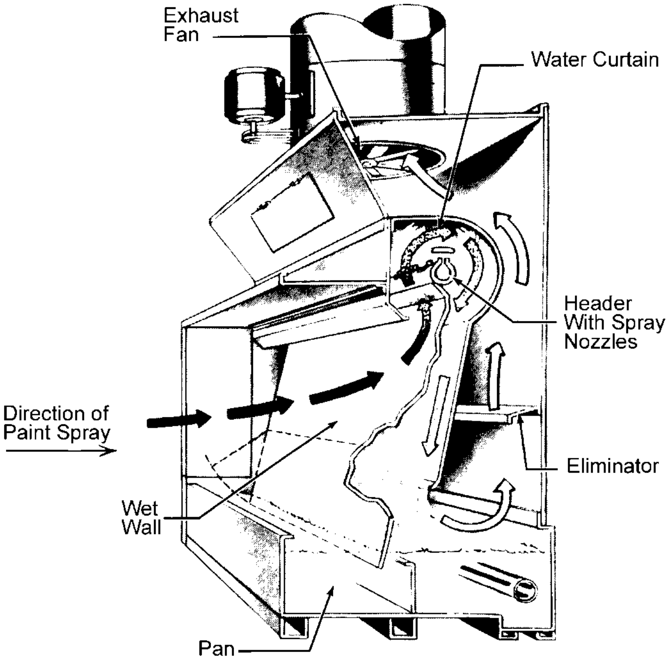

FIGURE 43.7 Small parts paint spray booth.

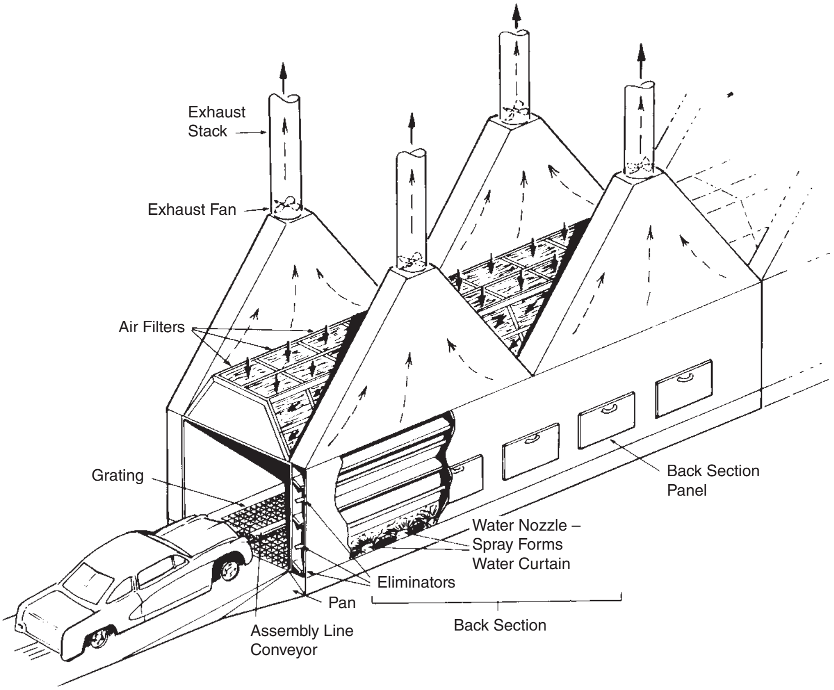

FIGURE 43.8 Automobile paint spray booth.

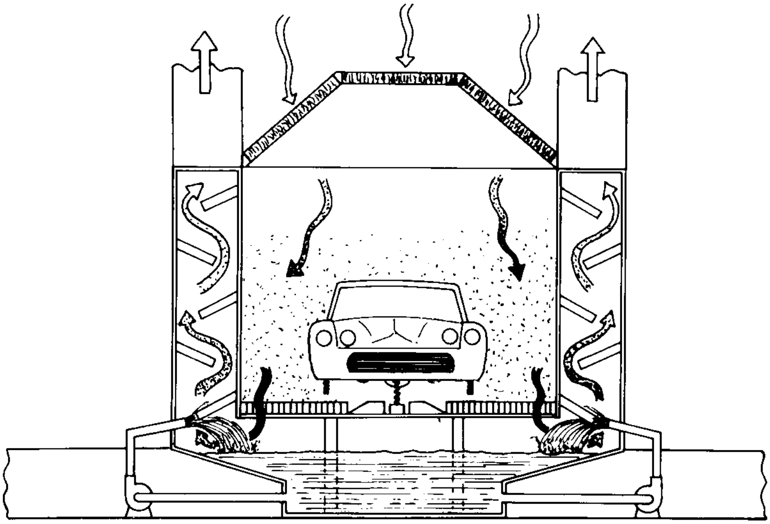

Figure 43.9 Cross section of automobile paint spray booth.

Detackifying Paint

Properly treated water will collect the pigment and organic components of the paint and condition these so that they are not tacky, producing a sludge that can be readily handled without sticking to the scrapers or flights used for removal. The material that carries up into the back section is scrubbed out and killed by properly designed and treated water wash, so that deposits do not form in this relatively constricted wall cavity. If the scrubber is not performing properly, particles penetrate the water curtain, build deposits in the back sections, and go out the stack as particulate emissions. In addition to the air pollution problem, extensive maintenance is required to remove the deposits in the back sections, on the eliminators, on the fan blades, and in the basin below the grating to keep the booth operating, so that it provides safety to the operator and a clean discharge to the outside air.

Paint spray booths are in some respects like an air washer, in that the spray water may evaporate and cause concentration of dissolved solids, or water may be condensed from the air, resulting in dilution of the spray water. This means that a check on total dissolved solids (TDS), pH, and alkalinity is required periodically to keep the system under good control.

Recirculation volumes on booths of this type are high, about 10 000 gpm (2270 m^3/h) for a typical body spray booth and 500 to 1000 gpm (114–227 m^3/h) for a parts spray booth. The basin is usually dumped once or twice per year. The actual makeup water requirements are difficult to estimate, because they depend on the evaporation rate and the frequency of dumping, which are unique for each installation.

Stamping

In preparation for stamping, the first step is to loosen mill scale from the metal surface by passing the strip steel through a flex roller (Fig. 43.10). This flex roller bends and flexes the steel through a series of rollers. Wash oil is brushed on during the flexing operation to remove the mill scale and dirt.

The flexed steel is cut to size and then stamped to the desired shape by large hydraulic presses. Drawing oil is sprayed on the dies to aid in stamping.

The stamped part is further cut and trimmed to the precise size, and the drawing oil, cutting oil, and dirt are removed in a parts washer, creating an oily wastewater. The part may then be welded or primed, depending on the manufacturing requirements. The assembled part is then ready for shipment to the assembly plant. Finished products from stamping and fabrication plants include doors, floor pans, trunks, hoods, and fenders.

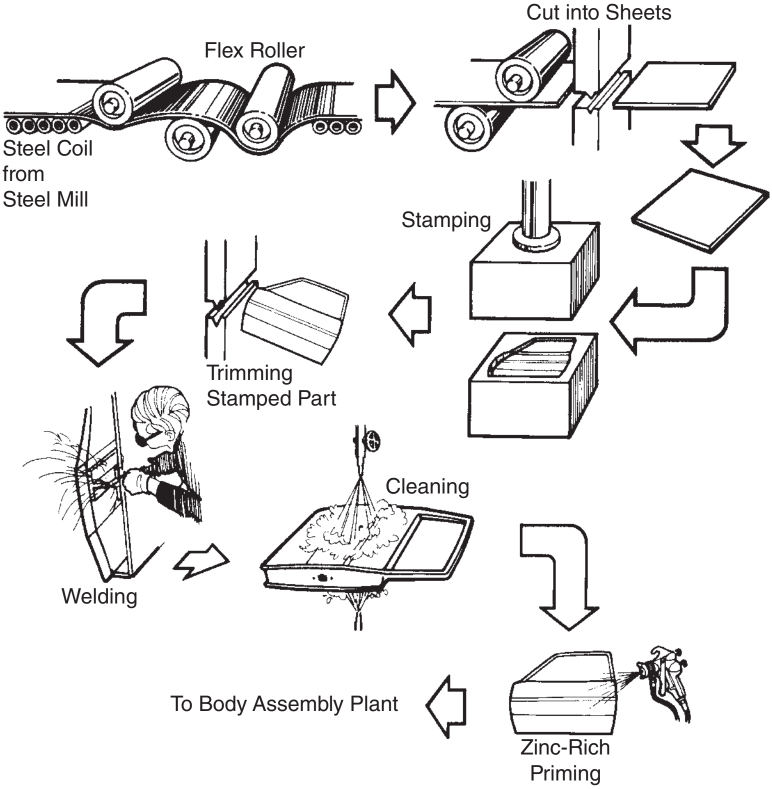

FIGURE 43.10 Fabricating and stamping.

The flows from stamping and fabrication are usually quite low [50 000 gpd (189 m^3/d)] and consist of oily wastes from the parts washers, cooling water blowdown, and blowdown from the spray booths. The wastewater contains 100 to 500 mg/L oil and can be effectively treated with oil–water emulsion breakers. Occasionally, wash oil, hydraulic oil, and drawing oil are sent to the waste plant, but most plants try to segregate these relatively clean oils from the wastewater for recovery or sale.

Plating Wastes

Where plating of parts is a major operation, waste treatment plants are designed to remove heavy metals. Traditional treatments of reduction and pH adjustment to remove the metal as its hydroxide are commonly used. A typical heavy metal removal plant is shown in Fig. 43.11. Destruction of cyanide may also be required.

Economics may justify heavy metal recovery, most frequently by an ion exchange operation. Nickel is easily reclaimed from rinse tanks following nickel plating on acid regenerated cation resin, with the nickel-rich regenerant returned to the plating tank. Chromium is also recoverable, but not in a form useful in the plating operation.

Plating is as much an art as a science. Parts to be plated require careful cleaning and rinsing, often with soft water to avoid spotting. The plating baths are precisely controlled and may require demineralized water makeup. A typical plating line is shown in Fig. 43.12.

Painting is increasingly important in the metal fabrication plants, as the efforts to stop body corrosion increase. Zinc-rich primers are sprayed on the interiors of doors, fenders, and other areas that are enclosed after assembly to improve corrosion protection. This operation is performed in the same type of spray booth described earlier.

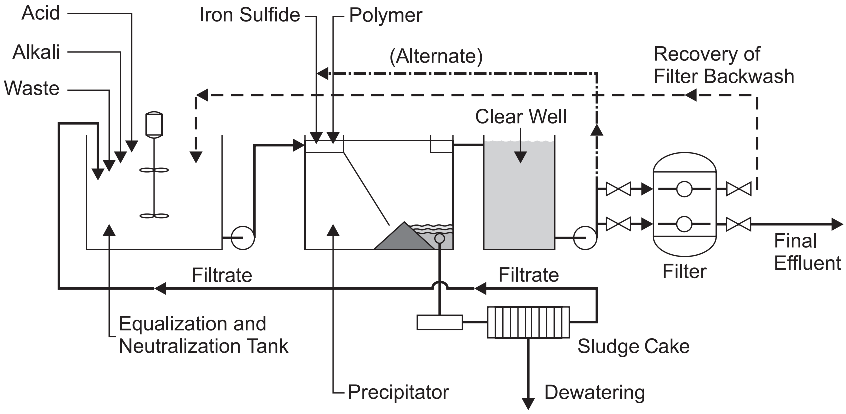

FIGURE 43.11 Heavy metals precipitation in a metal finishing shop using sulfide precipitation.

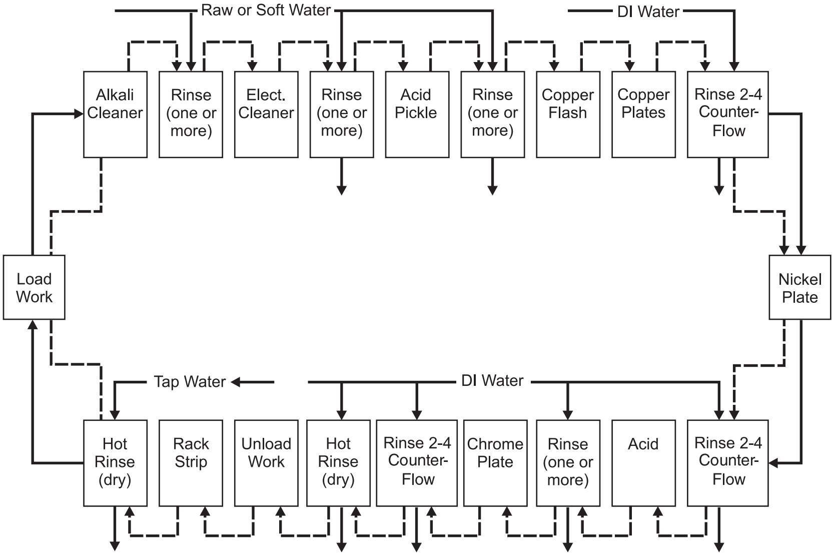

FIGURE 43.12 Flow sheet for a chrome plating line, including cleaning step and three stages of metal deposition.

Utilities, such as steam and cooling water, are much the same in stamping and fabrication as described for the machining operation.

Assembly Plants

Figure 43.13 shows a typical flow diagram for an assembly plant. These plants receive all of the parts and subassemblies produced in supplier plants and assemble them into a finished car. Major operations include welding, bonderizing, painting, and assembly.

In the assembly plant, the sheet metal is welded to the frame and floor pan to construct the shell of the car. During the welding operation, the welder tips are cooled by recirculating water. The most common problem in this closed cooling system is fouling, which plugs the tips with corrosion products. If the water flow is reduced by plugging, the tips will overheat or even melt, causing a shutdown of the assembly line. Filtration and chemical treatment with conventional corrosion inhibitors minimize this corrosion and plugging.

In the bonderizing step, a metal phosphate layer, such as zinc phosphate, is applied to the metal surfaces to provide corrosion protection and a surface for the paint finish. Figure 43.14 shows a typical phosphatizing operation consisting of cleaning, rinsing, phosphating, rinsing, and sealing. After bonderizing, many plants use a process called electrodeposition to electrostatically deposit a primer coat of paint on the metal surface, by dipping the electrically charged metal into a vat of

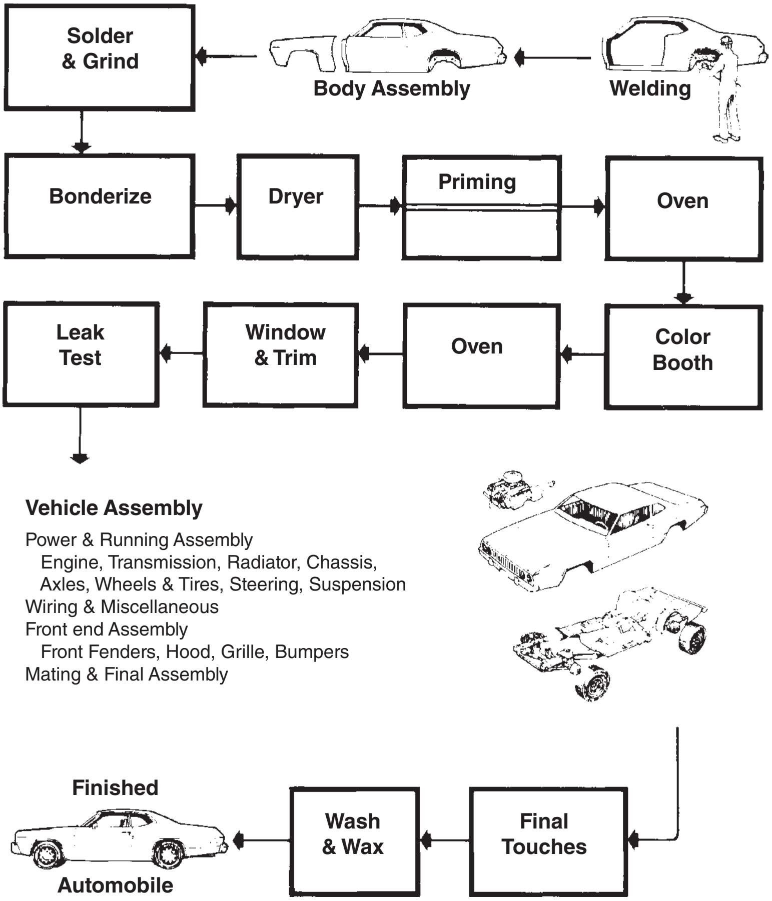

FIGURE 43.13 Process flow in an automobile assembly plant.

water-based paint. The oppositely charged paint particles are attracted evenly to the metal surface (Fig. 43.15). Makeup to this system is demineralized water, so that the bath conductivity can be controlled.

In this process, the bath tends to heat up. The paint is cooled below 90°F (32°C) through a heat exchanger by either a chiller or an open recirculating cooling tower system. After the electrostatic dip, the painted car is baked in an oven to set the finish. The exhaust gases from the oven pass through heat exchangers to recover heat by warming the oven makeup air. These exchangers foul with paint residue and require frequent cleaning.

Periodically, concentrated rinse water from electrostatic coating is discharged to the waste treatment plant. These discharges can upset the waste plant by introducing waste that is difficult to treat. If the pH of the electrocoat paint is increased above 6.0, large sticky deposits

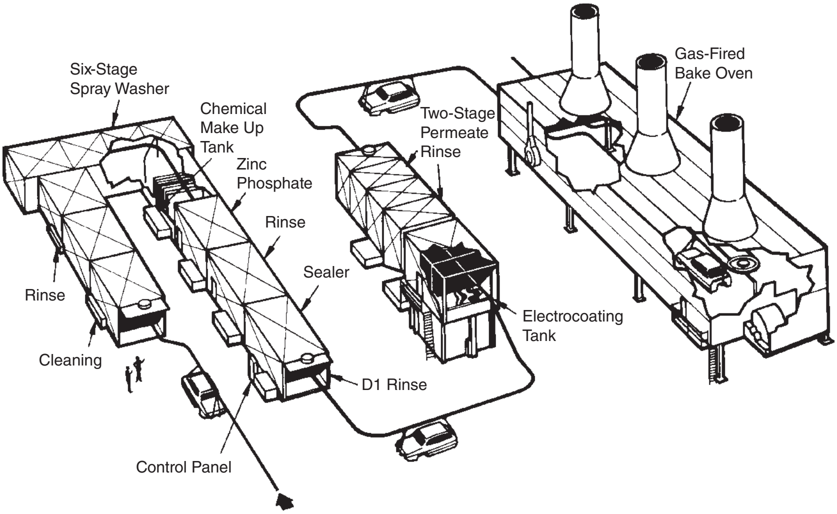

Figure 43.14 Phosphating and electrocoating lines.

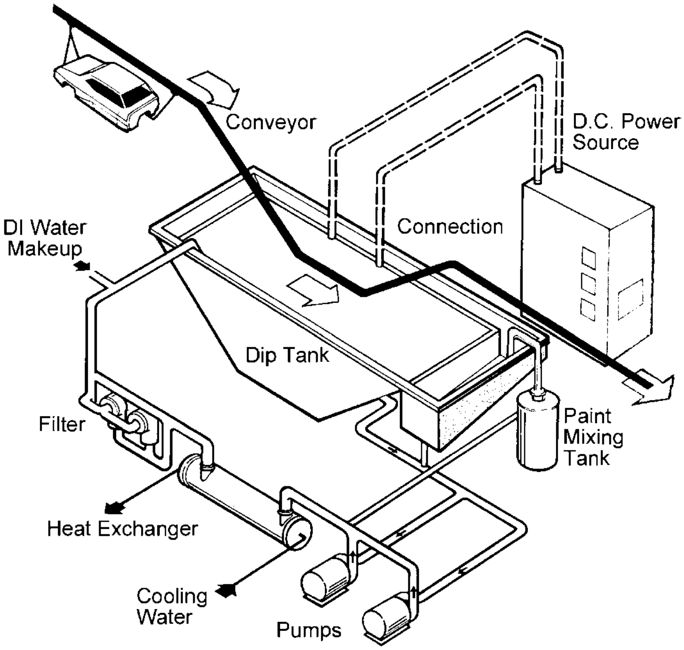

Figure 43.15 Electrocoating process for automobile bodies.

form and plug the lines and pumps. If the pH of the electrocoat paint is reduced below 3.5, a tar-like substance will form and plug the lines and pumps.

Most vehicle assembly plants have the type of wet spray booths described earlier.

There are two specific miscellaneous water uses in the assembly plant:

1. The assembled car is passed through a spray to test for leaks. Fluorescent dye is put in the water so a black light will clearly reveal leaks. Wetting agents are also added to make the test more severe and to prevent water spots.
2. The final process is a typical car wash operation. Various soaps are added to help clean the car.

Wastes from assembly plants are usually quite similar. Typical contaminants are oil, BOD, SS, zinc, nickel, phosphate, and sometimes paint sludge. Coagulants and oil-in-water emulsion breakers work well on these waters. Water comes from spray booths, stripping tanks, phosphatizing, wet sanding, car wash, cooling water, leak test, and various parts washers. Typical flows range from 500 000 to 1 000 000 gpd (1890–3790 m^3/d).

Table 43.3 summarizes water uses in the major automotive manufacturing steps.

	Foundry	**Machining**	**Fabricating and Stamping**	**Assembly**
Cooling	Cupola walls Cupola wet cap Slag granulator Comfort Compressors Furnace walls	Engine testing Oil coolers Comfort Compressors	Stamping Welder Comfort Compressors	Welder Priming Comfort Compressors
Boilers	Makeup Wet scrubbers	Makeup Wet scrubbers	Makeup Wet scrubbers	Fuel Internal
Cleaning		Makeup Rinse	Makeup Rinse	Makeup Rinse
Spray booths		Makeup	Makeup	Makeup
Plating			Makeup Rinse	

TABLE 43.3 Summary of Water Uses

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CHAPTER 44

The Municipal Sector

Communities differ widely in character and size, but all have common concerns of finding, treating, and distributing water for industrial, commercial, and residential use. Residential uses include washing, transporting wastes, drinking, food preparation, watering lawns and gardens, heating and cooling, and fire protection. According to the U.S. Environmental Protection Agency (EPA), there are 156 000 public drinking water systems in the United States. Although the common purpose is water treatment, systems vary widely. Groundwater systems are more prevalent than surface water, but more people drink water from surface water systems.

Because water is so basic to life, public interest in governing water quality has been strong. This has created a demand for modern treatment plants, trained operators, and careful inspection of chemical treatment and water quality. Consumption of water per capita ranges from approximately 100 gpd (0.38 m^3/day) in very small municipalities to about 200 gpd (0.76 m^3/day) in larger systems having greater industrial and commercial demand. Water use primarily depends on availability of water resources, climatic and seasonal variations, and cost of finished water. Where water is scarce, it is used only for essential purposes. Where cost is a prominent factor, it primarily restricts nonessential uses of water such as lawn watering, since essential uses are served regardless of cost.

EPA broadly categorizes water users and volumes used in the United States as follows:

1. Domestic
2. Power plants
3. Agriculture
4. Industrial and mining

Domestic—Water is used for residential, commercial, industrial, and public uses such as street cleaning, firefighting, municipal parks, and public swimming pools. This includes both publicly supplied sources (water delivered by a public or private system) and self-supplied sources (water withdrawn directly from surface or groundwater, such as from privately owned wells). Fifteen percent of American households are self-supplied, while more than 240 million people depend on public supply systems. Withdrawals for public supply systems total more than 43 billion gpd (163 million m^3/day). Historically, nearly 60% of public supply is delivered to households. Self-supplied water to households totals nearly 4 billion gpd (15 million m^3/day).

Power plants—Water is used during production of energy from fossil fuel, nuclear, or geothermal sources. Most water withdrawn for power plants is used for cooling purposes; power plants use 136 billion gpd (515 million m^3/day) of freshwater.

Agriculture—Water is used to irrigate farm crops and for livestock, dairies, feedlots, fish farms, and other farm needs. Agricultural irrigation accounts for more than 142 billion gpd (538 million m^3/day) of freshwater.

Industrial and mining—Water is used for cooling in factories and washing and rinsing in manufacturing processes. Some major water use industries include mining, steel, paper, chemicals, and associated products. Industrial facilities withdraw more than 20 billion gpd (76 million m^3/day) of freshwater.

Disinfection

Water has been treated before use for thousands of years by a variety of processes. Methods of water treatment are illustrated in early Greek and Sanskrit writings and include descriptions of filtering through charcoal, straining, and boiling. As early as 1500 B.C., Egyptians used alum (aluminum sulfate) to clarify water. During the 18th century, filtration was established to remove particles from water, and by the next century, sand filtration was employed in Europe. It was not until the 19th century that it was evident many serious epidemics was associated with contaminated water. In the early 20th century, discoveries centered on disinfectants such as chlorine and ozone that could destroy pathogenic (disease causing) organisms. At that time, chlorine was used in the United States and ozone predominantly in Europe.

NSF International, founded in 1944 as the National Sanitation Foundation, is known for the development of standards, product testing, and certification services in the areas of public health, safety, and protection of the environment. According to NSF, the majority of public utilities in the United States uses some form of disinfection to protect against pathogens in drinking water supplies. In the 21st century, the most common disinfection techniques are: chlorine, ozone, ultraviolet (UV) light, chloramines, and chlorine dioxide. Scientific research has found that by-products (called disinfection by-products or DBP) can form when some of these disinfectants react with natural organic matter (NOM) such as decaying vegetation. DBP also form when certain compounds such as bromide are present in source water.

Although studies are being conducted to determine potential health effects of DBP consumed by humans over long periods, EPA has already set monitoring requirements and maximum contaminant levels (MCL) for some of the more common by-products, including trihalomethanes (THM), haloacetic acids (HAA), bromate, and chlorite.

Chlorination By-Products

During the 1970s, scientists discovered a possible origin of DBP from disinfectant reaction with organic matter. Subsequently, research ensued to study health effects and develop measures to prevent formation of these products during the disinfection process. Formation of DBP generally takes place by chlorine reacting with organic substances, such as humic and fulvic acids, generically called total organic carbon (TOC) or NOM. These materials enter water during decomposition of plant matter. Literature provides little information on the complex chemical structures of humic and fulvic acids, and the mechanism of DBP formation remains unclear. Because of the extensive number of substances that make up NOM, research is difficult.

Formation of THM and HAA is temperature and pH dependent. Under conditions with extended reaction time, transitory DBP may become disinfection end products. At elevated temperatures, reaction rates are faster, and greater chlorine dosages are required for adequate disinfection, thereby producing halogen by-products. A delicate balance is required to optimally treat drinking water.

When pH values are high, more hypochlorite ions are formed, causing effectiveness of chlorine disinfection to decrease. At higher pH values, more THM are formed, whereas more HAA are formed when pH values are lower.

Chlorine

Chlorine (Cl_2), in the form of hypochlorous acid (HOCl), is one of the most widely used forms of disinfection for drinking water in the United States today. Chlorine is effective at deactivating many forms of pathogenic bacteria and viruses. Chlorine gas is yellow-green in color and added to water to form hypochlorous acid. The gas itself can be pressurized and cooled to a liquid, so that it can be shipped and stored. Sodium hypochlorite (NaOCl), formed from chlorine and sodium hydroxide, is also used to disinfect public water supplies but does not have the added hazardous chemical storage constraints of chlorine gas.

Chlorine is less effective at treating other microorganisms such as parasites. Because parasites or cysts such as *Cryptosporidium* and *Giardia* have a protective outer shell, chemical disinfectants such as chlorine do not penetrate and deactivate these microorganisms well.

Chlorine reactions are temperature and pH dependent. Chlorine works best in water with a low pH and a high temperature. Free residual chlorine (FRC) is the disinfectant that has not combined with chemicals, microorganisms, and plant material found in the water. Chlorine dosage must be adequate to meet chlorine demand and provide a measurable residual at the end of the water distribution system.

Chlorine has been found to react with NOM in source water to form DBP. THM include chloroform, bromoform, bromodichloromethane, and dibromochloromethane. The EPA has regulated the maximum annual average of total trihalomethanes (TTHM) detected in local water supplies to less than 80 μg/L. Haloacetic acids include five acids (HAA5): monochloroacetic acid, dichloroacetic acid, trichloroacetic acid, monobromoacetic acid, and dibromoacetic acid. Currently, EPA has regulated the maximum annual average of HAA5 to less than 60 μg/L.

Ozonation

Ozone (O_3) has been used for many years at bottled water production facilities and public water treatment facilities, particularly in Europe, for disinfection. This type of disinfection super oxygenates water, which kills many forms of bacteria and parasites. Ozone does not leave a disinfection residual in the water; therefore, most water utilities combine the use of ozone with another disinfectant such as chlorine to help maintain microbiological quality of water throughout the distribution system.

If bromide ion (Br^-) is present in source water and ozone is used for disinfection, a chemical known as bromate (BrO_3^-) can form. EPA has determined that bromate may pose a health risk, and utilities using ozone must monitor for bromate and maintain a maximum annual average of less than 10 μg/L.

Chloramines

Chloramines are becoming more prevalent as disinfectants in drinking water systems. Chloramines, a combination of chlorine and ammonia, have been widely and successfully used as a drinking water disinfectant since the 1930s. Generally, chloramines are used to maintain chlorine residuals in large distribution systems because of longer stability relative to chlorine alone. EPA estimates that more than half of U.S. large water systems currently use chloramines. Major U.S. cities, including Denver, Boston, Indianapolis, St. Louis, Portland, and Minneapolis, use chloramines.

Because of concerns about DBP, some communities have switched from chlorine to chloramines for disinfection. Chloramines do not react as readily with organic matter, thereby reducing potential DBP formation.

Chlorine Dioxide

Chlorine dioxide (ClO_2) can be used for disinfection purposes. DBP may also form when utilizing chlorine dioxide for disinfection. EPA currently requires utilities using chlorine dioxide to monitor the water for chlorite (ClO_2^-).

Fluoridation

In 2000, the U.S. Centers for Disease Control and Prevention (CDC) estimated that 66% of residents using community water systems (162 million people) had access to fluoridated tap water. Since 1945, North American water systems have added fluoride, a naturally occurring element, to water supplies to help prevent tooth decay. According to the American Water Works Association (AWWA), since that time child cavity rates have been reduced by 20 to 40%, where fluoridation has been implemented. Fluoridation of drinking water is endorsed by the American Dental Association, the American Medical Association, and the U.S. Public Health Service. CDC proclaimed fluoridation to be one of the top ten greatest public health achievements of the past century.

U.S. Regulatory History

Federal regulations pertaining to water treatment began in 1914 when the U.S. Public Health Service set standards on the bacteriological quality of water. The standards were revised in 1925, 1946, and 1962. The 1962 standards regulated 28 substances and were the most robust standards until the Safe Drinking Water Act (SDWA) of 1975, when EPA was mandated to institute a new system of quality regulations. Interim primary (enforceable) standards became effective in July 1977. This law was significantly amended in 1986 and 1996.

Proposed in 1994, the SDWA Amendments of 1996 required EPA to comply with the regulatory timeline it set forth in its initial Disinfectant and Disinfectant By-product Rule (DDBPR) and Interim Enhanced Surface Water Treatment Rule (IESWTR). Amendments to the SDWA in 1996 require EPA to develop rules to balance risks between microbial pathogens and DBP to increase defense against microbial contaminants, especially *Cryptosporidium*, while simultaneously reducing potential health risks of DBP. The Stage 1 DDBPR and IESWTR, announced in late 1998, are the first of a set of rules under the 1996 SDWA Amendments. Stage 1 of DDBPR established the following course of action:

- Establishes a goal of completely removing the top four THM from U.S. water supplies
- Reduced acceptable level of TTHM by 20%
- Introduced a new group of DBP, HAA5, for regulation
- Requires water suppliers to reduce levels of TOC, which react with disinfectants to make DBP
- Requires levels of disinfectants in water after disinfection to be reduced

Stage 2 of DDBPR was released in January 2006. Stage 2 focuses on public health protection by limiting exposure to DBP, specifically TTHM and the HAA5. Exposure is limited by removing TOC from finished water based on raw water TOC and alkalinity levels (see Table 44.1).

The EPA establishes MCL for those contaminants known to cause, or suspected of causing, health problems. MCL defines the highest concentration allowed in public water supplies.

Water may be safe to drink but have an undesirable taste, odor, or color. Some water may stain clothes and fixtures, corrode plumbing, or form a scale and film. Secondary maximum contaminant levels (SMCL) are often recommended by EPA for these aesthetic water quality factors. SMCL are useful guidelines for evaluating suitability of water for drinking, bathing, clothes washing, cooking, and other domestic uses.

For a current list of MCL and SMCL, the reader is directed to the EPA web site.

In some cases, requirements of the SDWA necessitate a change to a more acceptable water source. Implementation of the SDWA Act

Source Water TOC (mg/L)	**Source Water Alkalinity (mg/L as $CaCO_3$)**		
	0–60	60–120	>120
2–4	35%	25%	15%
4–8	45%	35%	25%
>8	50%	40%	30%

Table 44.1 Required Removal of TOC by Enhanced Coagulation and Enhanced Softening for Systems Using Conventional Treatment

has resulted in consolidation of many small water suppliers into larger regional systems to take advantage of economy of scale.

Cryptosporidium and *Giardia*

Cryptosporidiosis is a diarrhea disease caused by microscopic protozoan or single-celled parasites, which live in the intestines of animals and humans. Both the disease and the parasite are commonly known as "Crypto." *Cryptosporidium* was first discovered as a cause of human disease in 1976 but was rarely reported in humans until 1982.

A hard outer shell protects the parasite and allows its inactive (dormant) form or oocyst to survive outside the body for long periods. The hard outer shell also makes it very resistant to chlorine disinfection.

While this parasite can be transmitted in several different ways, water is a common method of transmission, and *Cryptosporidium* is one of the most frequent causes of waterborne disease (drinking water and recreational water) among humans in the United States. Conventional treatment techniques including filtration and adequate chlorine contact time are most appropriate to inactivate the oocyst.

Groundwater usually has good microbiological quality, because it passes through various geologic layers in the ground, which function as a natural filter. Afterwards, water still requires disinfection because groundwater, especially shallow groundwater, can be contaminated by sewage or wastewater.

Untreated surface water can infect humans with *Cryptosporidium*, as the origin is from animal waste that enters municipal drinking water intakes. Oocysts are present in most surface waters in the United States, and concentrations are exacerbated during heavy rains because of runoff of animal wastes from land and overloaded wastewater treatment facilities.

In 1987, 13 000 people in Carrollton, GA became ill with cryptosporidiosis. In 1993 in Milwaukee, WI, 400 000 people fell ill from using drinking water that was contaminated by *Cryptosporidium* cysts. These outbreaks directed attention to waterborne diseases and the need for more stringent drinking water standards.

Cryptosporidium is chlorine resistant due to its hard outer shell, and therefore, multiple methods are required to protect public water supplies. Watershed protection, filtration, and disinfection are all used in combination to protect drinking water. Additionally, UV light and ozone are capable of inactivating the parasite, the latter with adequate contact time. The EPA standard requires 99% removal of *Cryptosporidium* for public drinking water systems.

Other pathogenic microorganisms that can be found in drinking water are *Escherichia coli*, caliciviruses, *Helicobacter* bacteria, *Mycobacteria*, and *Giardia lamblia*. In the future, more pathogenic microorganisms will likely emerge and spread through water because of increased agricultural activities, population growth, migration, and climate change. Pathogenic microorganisms can also emerge because they develop resistance to disinfectants.

Giardiasis is a diarrhea illness caused by a single cell microscopic parasite, *Giardia intestinalis* (also known as *Giardia lamblia*). Once an animal or person has been infected with *Giardia intestinalis*, the parasite lives in the intestine and is passed in the stool. Because an outer shell protects the parasite, it can survive outside the body and in the environment for long periods.

Since the late 20th century, *Giardia* infection has become recognized as one of the most common causes of waterborne disease (found in both drinking and recreational water) in humans throughout the United States.

The *Giardia* parasite lives in the intestine of infected humans or animals. Millions of parasites can be released in a bowel movement from an infected human or animal. *Giardia* is found in soil, food, water, or surfaces that have been contaminated with feces from infected humans or animals.

Tests used to specifically identify *Giardia and Cryptosporidium are* often expensive, difficult, and usually require large volumes of water to be pumped through a filter.

The primary disinfectant used in the United States is chlorine. In order to be effective and inactivate oocysts and *Giardia*, adequate contact time is required. Contact time depends on the temperature and pH of water. Chlorine works best in water with low pH and high temperature. Concentration and contact time required to inactivate *Giardia* using chlorine is approximated by Eq. (44.1).

$$\mathrm{CT} = 0.2828(\mathrm{pH}^{2.69})(\mathrm{FRC}^{0.15})(0.933^{(T-5)})(L) \tag{44.1}$$

where CT = contact time in, min
pH = pH of water
FRC = free residual chlorine, mg/L Cl_2
T = temperature, °C
L = log removal

The CT concept was developed specifically for surface water, assuming that water treatment focuses on inactivating both *Giardia* and viruses. CT required to provide 3-log inactivation of *Giardia* is at least enough to provide the required 4-log inactivation of viruses; therefore, EPA just set the standard for *Giardia*.

An example of the discussion above would be the determination of the CT required for a 3-log inactivation at a chlorine residual at 1 mg/L and a water pH. of 8.0 with a 10°C temperature. Substituting the variables into the equation we can determine that 161 minutes of contact time is required.

$$\begin{aligned}\mathrm{CT} &= 0.2828(8^{2.69})(1.0^{0.15})(0.933^{(10-5)})(3) \\ \mathrm{CT} &= 161\,\mathrm{min}\end{aligned} \tag{44.2}$$

Raw Water Characteristics

Raw water characteristics vary widely, the major differences being between surface and groundwater, hard and soft water, and river water compared to reservoir water. These differences present varying needs for algae control, turbidity removal, softening, water stabilization, and disinfection.

Generally, water supplies within a defined geologic region are similar. There has been a trend to use surface water because of its availability, and it minimizes risks of earth subsidence due to uncontrolled groundwater withdrawal. Raw water with a constant low turbidity has more treatment options than one of high or variable turbidity. The presence of color in many low alkalinity waters requires special treatment considerations.

Corrosion and Scale

Corrosion in distribution system pipes occurs through electrochemical action and is the reversion of refined metals back to their natural state. The electrochemical cell consists of an anode (site of oxidation) and a cathode (site of reduction). Electrolytic solution (water) connects the anode and cathode. Metal enters solution at the anode, while the cathode attracts electrical current and collects atomic hydrogen. Proper corrosion control methods disrupt one or more of the corrosion cell reactions to reduce the extent of metal release.

To control corrosion in drinking water distribution systems, chemical treatment recommendations and dosage requirements must consider an overall system approach. All waters are corrosive to some degree. Chemical characteristics of water and metallurgy of materials it contacts determine how aggressive the water is. Raw water supplies and treatment schemes vary considerably, resulting in waters with aggressiveness from mild conditions causing negligible attack, to antagonistic conditions causing rapid deterioration. Factors affecting corrosiveness of potable water in distribution systems are dissolved gases, temperature, bacteria, pH, and dissolved ions.

Raw water sources vary with respect to dissolved gases. Some groundwater contains carbon dioxide (CO_2), which converts to carbonic acid (H_2CO_3) and produces pH less than 6. Other groundwater contains hydrogen sulfide (H_2S) that reacts with carbon steel and causes pitting from deposition of ferrous sulfide (FeS). Dissolved oxygen in both surface and groundwater sources is a major influence, since carbon steel corrosion is directly proportional to the oxygen content of water. While chlorine is a chemical used for biological control, excessive chlorination can increase the corrosion rate of steel.

Lead occurs in drinking water from two sources: lead in raw water supplies and corrosion of plumbing materials in the water distribution system (corrosion by-products). Most lead contamination is from corrosion by-products. Lead in drinking water results primarily from corrosion of materials located throughout the distribution system containing lead and copper, and from lead and copper plumbing materials used to plumb public and privately owned structures connected to the distribution system. The amount of lead in drinking water attributable to corrosion by-products depends on a number of factors, including the amount and age of lead and copper bearing materials susceptible to corrosion, how long the water is in contact with the lead-containing surfaces, and how corrosive the water in the system is toward these materials.

Potential sources of lead corrosion by-products found in drinking water can include: water service mains (rarely), lead goosenecks or pigtails, lead service lines and interior household pipes, lead solders and fluxes used to connect copper pipes, and alloys containing lead, including some faucets made of brass or bronze.

Most public water systems serve at least some buildings with lead solder or lead service lines. EPA estimates that there are about 10 million lead service lines/connections. About 20% of all public water systems have some lead service lines/connections within the distribution system.

The amount of lead in drinking water depends heavily on the corrosiveness of the water. All water is corrosive to metal plumbing materials to some degree, even water termed noncorrosive or water treated to make it less corrosive. Corrosiveness of water to lead is influenced by water quality parameters such as pH, total alkalinity, dissolved inorganic carbonate, calcium, and hardness. Galvanic corrosion of lead into water also occurs with lead-soldered copper pipes, due to differences in the electrochemical potential of the two metals. Grounding of household electrical systems to plumbing may exacerbate corrosion.

Corrosion Control

Based on work completed at New England water plants in the late 1930s, Calgon Corporation obtained a patent in 1943 for the use of sodium hexametaphosphate (SHMP) as a corrosion inhibitor. Polyphosphate combines with calcium in water to form a protective film on the metal pipe surface. Low levels of polyphosphate are fed to the finished bulk water supply that carries the chemical to the metal surface. As the action of flowing water sloughs off the established protective molecular film, it is replaced immediately. Therefore, sufficient polyphosphate must be fed to form a molecular film throughout the distribution system. The main function of the polyphosphate is to treat the metal surface and not the water itself; thus, a residual must be maintained at the end of the distribution system.

The use of "bimetallic" (sodium-zinc) glassy polyphosphate began in the 1950s. Addition of zinc enhanced performance of polyphosphate by increasing the rate at which the protective film is formed on the metal surface. It proved to be a more tenacious protective film than that provided by polyphosphate alone, particularly in low-flow or dead-end areas of the distribution system.

In 1970, zinc orthophosphate was used for corrosion control in a southern California potable water system. Orthophosphate is an anodic inhibitor, while zinc polarizes the cathode. This treatment is particularly effective in low alkaline, low hardness waters. It is also used in stifling the release of asbestos fibers into water flowing through asbestos-cement pipe. Zinc is the critical component in this treatment and can be obtained with zinc polyphosphate as well. However, care must be taken when hardness and alkalinity increase, because calcium orthophosphate can precipitate. In this case, the inhibitor is not available to protect the metal surface, and both corrosion and scale can occur.

With passage of the Lead and Copper Rule in 1991, many systems failed obtaining compliance with first draw samples of less than 15 μg/L of lead in 90% of samples. Use of orthophosphate can reduce lead solubility; however, lead is only one of the many different alloys in the distribution and household systems. Orthophosphate has been successful in bringing systems into compliance for lead, but it promotes steel pitting and has no efficacy for scale control or iron and manganese stabilization. Orthophosphate is being used as a corrosion inhibitor in such cities as the District of Colombia, Chicago, Richmond, New York City, and Detroit. Although available in several forms, orthophosphate can be added as phosphoric acid. A better alternative is either zinc orthophosphate or a poly/orthophosphate blend.

Blends of polyphosphate and orthophosphate are used increasingly for treating systems for corrosion control. Orthophosphate is an anodic inhibitor, while polyphosphate is a cathodic inhibitor. The product forms a protective molecular film and provides the added benefit of scale control, due to the polyphosphate portion of the product.

Sodium silicates are good for protecting iron and steel and particularly effective in hot water systems. Silicates require some initial corrosion to occur to form a protective film on the metal surface. It is self-limiting since the film stops developing when the corrosion products are no longer available. This film forms over clean or corroded surfaces. Usually, pH of the system is maintained in the range of 8 to 9.5. With high hardness waters, the higher the pH increases, the higher the potential for calcium carbonate scale. Since silicates cannot prevent scale, they should be used in soft water areas. In addition, with higher pH, there is the concern of chlorine effectiveness and TTHM formation.

Controlling corrosion is a complex process requiring water treatment system operators to be aware of all the issues of regulations, water quality, and water treatment scheme that affect performance of the selected program. Economic and aesthetic benefits are easily measured in lower maintenance and pumping costs, as well as fewer customer complaints. Meeting regulatory requirements at the tap allows treatment systems to lower the frequency and number of samples collected. This results in lower analytical costs as well as gaining consumer confidence, by never needing to notify them of being out of compliance.

Scale Control

Scale formation causes severe problems in potable water distribution systems. If untreated, raw water sources with high hardness levels can deposit calcium carbonate ($CaCO_3$) or calcium sulfate ($CaSO_4$) scale throughout the distribution system. In addition, accelerated corrosion can occur under the deposit, or the scale can provide a safe harbor for biological activity, which is sheltered from the disinfectant being used.

The result of scale formation is reduction in pipe diameter and increased pumping cost. Scale forms at the interface of the bulk water and distribution pipe. This solid/liquid interface is the site for crystal growth. At the interface, pH of water is higher than bulk water pH, because the oxygen–reduction reaction produces hydroxyl ions. Calcium carbonate solubility decreases with increased pH. In the homeowners hot water system, calcium carbonate scale forms due to increased water temperature, which decreases $CaCO_3$ solubility. Once solubility of the reaction product has been exceeded, scale deposition can occur.

There are several methods used to control scale in potable water systems: pH depression, softening via ion exchange or precipitation with lime and soda ash, as well as chemical treatment.

Modifying pH creates safety issues of handling strong mineral acids, and depending on the acid chosen, calcium sulfate or calcium phosphate scale can develop, magnifying scale problems. In addition, if not closely monitored, corrosive conditions can cause additional concerns, and one problem is just traded for another.

Total or partial softening to remove hardness is a more common practice to control scale formation. Softeners replace calcium and magnesium ions with sodium ions. This requires large quantities of salt (NaCl) to regenerate the resin when it has become exhausted. There is a high cost for the original equipment and the operating cost of handling concentrated spent brine from the regeneration process. Typically, large volumes of water are not processed through ion exchange equipment, since it reduces hardness to an extremely low level. Usually, the plant softens part of the water and blends it back with untreated water before sending it to the consumer.

Often, chemical precipitation with lime and soda ash (cold lime softening) is used to remove hardness and alkalinity. This treatment usually requires an extra step to add CO_2 after softening for recarbonation to reduce pH. Often times, the treatment process has two steps for solids removal: one for turbidity and one for precipitated hardness. This approach is effective but expensive. Handling dry lime and soda ash and monitoring chemistry to achieve the proper dosage to obtain desired hardness is labor intensive.

The simplest solution to control scale in potable water systems is to use polyphosphate as a "threshold treatment." The use of polyphosphate for scale control was developed by Calgon Corporation in conjunction with the U.S. Bureau of Mines in 1918 to prevent scale build-up in boilers. The technology was transferred to the municipal potable water treatment market in 1938, when SHMP was applied for scale control.

Polyphosphate controls scale by threshold treatment. This means that polyphosphate is used in substoichiometric quantities to control precipitation of scale. It uses a mechanism that retards nuclei formation as well as crystal growth. In raw water, calcium (Ca^+) and bicarbonate (HCO_3^-) are oppositely charged ions that are attracted and tend to form ion pairs. As they gather to create clusters, the polyphosphate molecule upsets equilibrium of the sub nuclei ion clusters, causing the ions to go back into solution. The polyphosphate molecule is available to upset this equilibrium on many groups of calcium carbonate clusters. Should clusters reach a subcrystallite or calcium carbonate stage, the polyphosphate molecule is attracted to the growth and inhibits further growth. With excessive calcium carbonate ions or low polyphosphate concentration, calcium carbonate crystals become deformed because of polyphosphate adsorption on the crystallite surface. Deformed crystals cannot grow and attach to surfaces, and are easily dispersed by flowing water.

Polyphosphate is manufactured by dehydrating orthophosphate in a furnace to form a linear chain structure. When adding it to water, it reverts to orthophosphate over time. For scale control, only polyphosphate protects the system. It has been found that both polyphosphate and zinc polyphosphate are effective scale control treatment schemes.

Since polyphosphate adheres to calcium carbonate surfaces, systems with high concentrations of scale build-up can use the dissolving and dispersing abilities of polyphosphate to eventually clean deposits from the system. Care should be taken when initiating treatment to prevent shocking the system and causing deposits to break away from pipe and accumulate in elbows and tees. Polyphosphate is used before mechanical cleaning to soften deposits in the system, so that the pigging operation is more effective. In addition, polyphosphates are used to keep filter media clean in softening plants by applying it to the influent water.

Typical Treatment Schemes

The type of treatment practiced at a given municipality depends largely on raw water characteristics. Wherever possible, water resources are acquired and maintained to require a minimum amount of treatment, thereby reducing the capital and operating costs to the municipality. Table 44.2 shows common impurities found in raw water supplies and examples of general types of treatment that can be employed. Which treatment is optimum depends on local conditions and the level of impurity.

A simple summary of various processes used for treating municipal water is shown in Fig. 44.1. By far, the largest number of municipalities simply uses the scheme shown by flow path 1, with water taken from a well, sterilized by chlorination, and pumped directly to the distribution system. Most systems like this are small and often operate with only part-time surveillance. Each state is responsible for reviewing the quality of water, both chemically and bacteriologically. In some cases, when this scheme is used, a chemical such as polyphosphate may be applied for final stabilization to minimize either scale or corrosion.

Often, low turbidity water should be clarified by direct filtration processes rather than by conventional coagulation and flocculation processes. This may significantly reduce the amount of sludge produced while maintaining water quality. Many plants with low raw water turbidity practicing conventional processes, apply chemical solids that far exceed the amount of suspended solids present in the raw water to be clarified. A more detailed explanation of coagulation and flocculation can be found in Chap. 6.

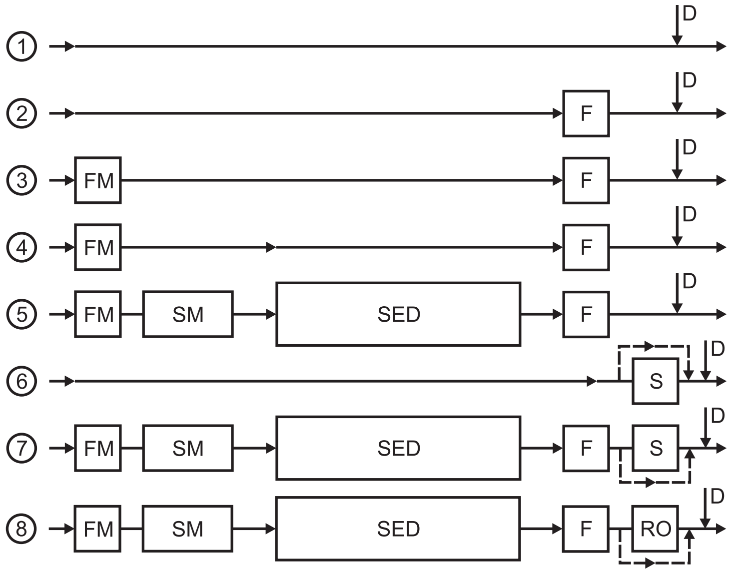
The second flow path shows only addition of a filtering system. In some old plants, the slow sand filter is still used for this purpose, but the rapid sand filter is now more commonly used. Because the sand filter is limited in its ability to handle suspended solids, this system is usually applied only to impounded waters of excellent quality, where post-chlorination can assure safe potable water. The filter may be installed to clarify shallow well water, where suspended iron may be an occasional problem. There are risks in this kind of system, because the filter does no more than removing suspended solids, which is seldom the only problem with a raw water supply.

The third flow path shows addition of an aerator before the filter for removal of tastes and odors and for oxidation of iron. Usually, this is followed by lime for pH increase to about 8 to 8.5 and a flocculant, since iron precipitate is usually colloidal.

In modern practice, the minimum equipment is usually considered that shown by flow path 4, and it is usually confined to impounded waters where there are consistently low suspended solids, depending on seasonal presence of algae and where final disinfection can assure safe finished water.

Treatment	Surface Water						Groundwater			Surface or Groundwater				
	Turbidity	Taste/ Odors	Hardness	Color	Fe/ Mn	Algae	Hardness	Fe/ Mn	H_2S	Bacteria/ Virus	Metals	Organics	Corrosion	Scale
Aeration		X			X			X	X					
Filtration only	X			X	X	X		X						
Ion exchange			X		X		X	X						
Lime softening	X	X	X	X	X	X	X	X						
Clarification/ filtration	X	X		X	X	X		X						
RO		X	X	X			X				X	X		X
Oxidation		X		X	X	X		X	X	X	X	X		
Chlorination		X		X	X	X		X	X	X	X	X		
Adsorption		X		X								X		
Phosphates													X	X
Zinc phosphates													X	

TABLE 44.2 Typical Water Impurities and Common Treatment Methods



Legend: A - Aerator, F - Filter, FM - Fast Mix, SM - Slow Mix, SED - Sedimentation Basin,
D - Disinfection, S - Softener, RO - Reverse Osmosis

FIGURE 44.1 Simplified schematic of municipal water treatment flow sheets.

In handling surface waters that contain significant suspended solids, the fast mix devices of flow path 4 are followed by a slow mix flocculator and a sedimentation basin in flow path 5, providing detention for settling most flocculated solids, so that load on the filter is measurably reduced. Detention can also provide for disinfection of raw water, with chlorine being added with or ahead of coagulation chemicals to relieve the final chlorine demand. The prechlorination step may improve flocculation by destroying some organic contaminants. This keeps settled solids from becoming septic and rising to the surface as gas forms.

In some cases, where water is already clear, the major problem may be caused by calcium and magnesium. In flow path 6, water is softened through ion exchange softeners. Some water is by-passed, so that the effluent can have hardness controlled at 100 to 150 mg/L as $CaCO_3$. Often, the cost of municipal softening is more than covered by savings to individual homeowners in areas where water is so hard that most homes would use individual softening units. A side benefit is reduced discharge of regenerant brine by the more efficient municipal plant.

Flow path 7 includes not only clarification of surface water but also final softening. In this scheme, the sedimentation tank may provide for lime softening as well as clarification, to reduce load on the ion exchange softening unit.

Finally, in flow path 8, the water plant includes tertiary treatment with reverse osmosis (RO) to produce exceptional quality water.

There are various other combinations of individual treatment processes incorporated into an overall treatment scheme, but the principles are generally little different from those illustrated.

Case History—Lake Bluff, IL

The Central Lake County Joint Action Water Agency (CLCJAWA) is a wholesale provider of drinking water for several communities in central Lake County, Illinois. The 1991 plant is composed of four identical treatment trains, has a total capacity of 50 mgd (131 m^3/min), and serves a population of approximately 200 000 (see Fig. 44.2).

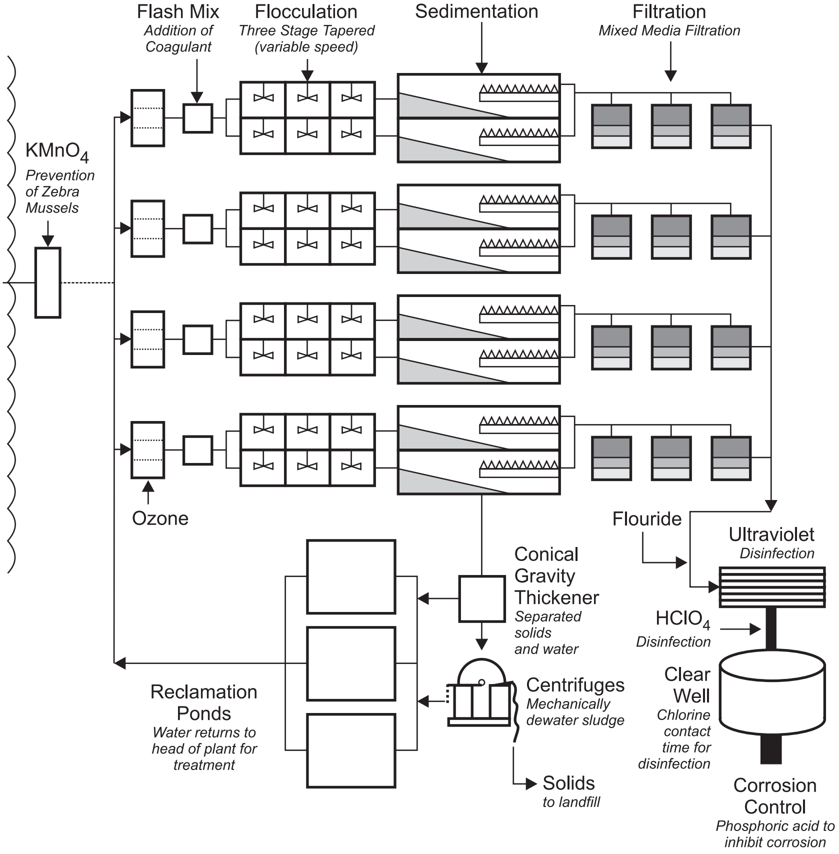


FIGURE 44.2 Lake County Illinois, plant schematic.

Treatment Process

CLCJAWA draws water from Lake Michigan. Potassium permanganate ($KMnO_4$) is added seasonally to inhibit mussel growth on the water plant intake and pipe. In the treatment plant, ozone is applied in ozone contactors for predisinfection, taste and odor minimization, and to enhance coagulation performance. Following ozone, coagulant is added in rapid mix basins. Water then flows through three consecutive flocculation basins, each basin mixed more gently than the previous to enhance floc size. Flocculated water then flows into settling basins equipped with inclined plate settlers. Here, floc falls a short distance to the inclined plate and rolls down the plate to the basin floor. Accumulated floc or sludge is removed twice daily using a chain and flight device to move solids to the sump of a telescopic valve. When lowered below the water surface, water pressure from the basin forces solids up and over the valve weir. Solids then flow to a processing facility equipped with gravity thickeners and centrifuges. Settled water flows upward through the bottom of perforated troughs that convey the water to filters. Once in the filters, water flows downward through 4 ft (1.2 m) of biologically active granular activated carbon, 1 ft (0.3 m) of sand, and either 1 ft (0.3 m) of gravel or a sintered plastic cap. Effluent from individual filters is collected, treated with fluoride, and conveyed to UV disinfection reactors. This process is followed by chlorination with sodium hypochlorite (NaOCl) and storage in two consecutive clearwells for a State mandated minimum of one hour before delivery. Phosphoric acid (H_3PO_4) is added at the head of the transmission system to control lead corrosion in resident's homes.

Treatment Chemicals

Potassium permanganate is added at an average dose of 0.2 mg/L. Ozone is produced on site using ambient filtered and dried air; average ozone dose is 0.8 mg/L. Average polyaluminum hydroxychlorsulfate coagulant dose is 7.1 mg/L, with historic maximum dose of 23.5 mg/L. UV light is dosed at 15 mJ/cm^2. Sodium hypochlorite dose averages 1.4 mg/L. This dose is lowered slightly in winter to maintain constant chlorine residual at the tap of approximately 0.5 mg/L. Average finished water free and total chlorine residual is 0.79 and 0.93 mg/L, respectively. Both fluoride and phosphoric acid are dosed to maintain constant residuals of 1.0 mg/L as F^- and 0.35 mg/L as PO_4^{-3}, respectively.

Typical Operations

Potassium permanganate is added when Lake Michigan water is above 50°F (10°C) or from May through October to discourage mussel attachment. Divers inspect the intake periodically to assure the practice is working as anticipated. Ozone is dosed to maintain a target residual of approximately 0.04 mg/L in the final contact basin. Adjustments to dose are dependent on water quality and flow rate through the plant. Besides raw water turbidity, coagulant dose is adjusted primarily based on filter effluent turbidity and by monitoring the time it takes for a filter to ripen following backwash.

Filters are backwashed when they reach a final head loss of 8 ft (2.4 m). Filter runs last from 40 hours in summer up to 300 hours in winter. The Supervisory Control and Data System (SCADA) automatically diverts filter flow from service when turbidity exceeds 0.10 NTU. Filter backwash consists of a 3-minute air scour and low wash, 5-minute-high wash, and 12-minute final low wash. Plant flow is adjusted to maintain water levels in three 3.5 million gallon (13 000 m^3) standpipes. Table 44.3 shows typical raw and treated water quality.

Membrane Filtration in Drinking Water Systems

Membrane filtration in drinking water applications can employ microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), or RO (see Fig. 44.3). According to the American Membrane Technology Association (AMTA), low-pressure MF and UF have emerged as viable options for addressing current and future drinking water regulations related to treatment of surface water, groundwater under the influence of surface water, and water reuse applications for microbial and turbidity removal. Both MF and UF have been shown to exceed removal efficiencies identified in the EPA Surface Water Treatment Rule and related rules, such as *Cryptosporidium* oocyst, *Giardia* cyst, and turbidity. Membrane filtration is becoming popular for conventional plant retrofits, replacing sand media for enhanced water quality and capacity increase. Membranes have shown success removing TOC, reducing potential for TTHM formation.

MF and UF membrane systems typically use hollow fibers that can be operated in the outside-in or inside-out direction of flow. The typical operational transmembrane pressure (TMP) of 5 to 35 psi (34–241 kPa) or vacuum [3–12 psi (21–83 kPa)] for outside-in membranes only) is the driving force across the membrane. TMP is the difference obtained when subtracting the filtrate pressure from the feed pressure. Typical flux (rate of finished water permeate per unit membrane surface area) at 68°F (20°C) for MF and UF ranges between 15 and 35 gallons per square foot per day (gfd) [2–4 m^3/(d · m^2)].

Disinfection is recommended after membrane filtration as a secondary pathogen control barrier, and for distribution system protection. Automated periodic backwashing and chemical washing processes are used to maintain the rate of membrane fouling within acceptable limits.

Chemical cleaning is employed once a maximum TMP differential has been reached. Some systems utilize air/liquid backwash. Typical cleaning agents include acids, caustic, surfactants, enzymes, and certain oxidants, depending upon membrane material and foulants

	Temperature	Turbidity	pH	Alkalinity	Hardness	Conductivity	TOC	Coliform Bacteria
Water	°F (°C)	NTU		mg/L $CaCO_3$		μS/cm	mg/L	MPN/100 mL*
Raw	50 (10)	8.2	8.32	106	128	296	2.1	192
Finished	NA	0.04	7.81	104	124	304	1.7	0

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*Most probable number per 100 mL

Table 44.3 Average Water Quality for Lake Bluff, IL Water Treatment Plant

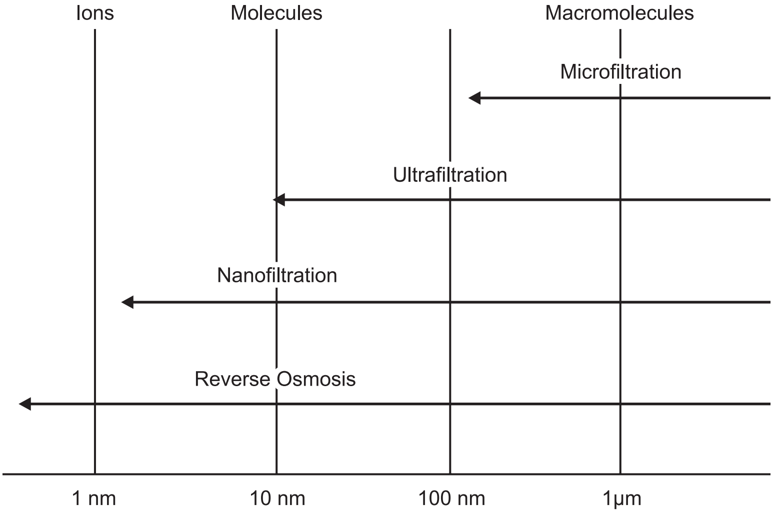

Figure 44.3 MF, UF, NF, and RO pore size comparison.

encountered. Chemicals used for cleaning and the method used in the cleaning process must be acceptable to the membrane manufacturer.

NF and RO are used to remove salts from seawater or brackish water. NF and RO membranes do not work according to the principle of pores but rather separation takes place by diffusion through the membrane. Pressure that is required to perform NF and RO is much higher than pressure required for MF and UF, while produced volume is much lower (higher reject flow). NF is a lower pressure RO and is referred to as "membrane softening." NF has been successfully used to treat hardness, high color, and high organic content feedwater. Compared to RO membranes, the NF membrane has lower monovalent ion rejection properties, making it more suitable to treat waters with low salinity, thereby reducing post-treatment requirements. The NF membrane works as an absolute barrier for cysts and most viruses. NF plants typically operate at 85 to 95% recovery. Brackish water RO plants typically transfer 70 to 85% of source water into permeate, and seawater RO recovery rates range from 40 to 60%. Further discussion of RO can be found in Chap. 8.

Membrane filtration has several benefits over conventional drinking water treatment techniques:

- Acceptable treatment possible at low water temperatures
- Simpler pathogen removal
- Low energy costs
- Process easily expanded as units are delivered in skids

To make drinking water from brackish water or seawater, a combination of UF followed by RO can be very cost-effective. UF cartridges used as pretreatment can significantly extend the useful life of RO elements. When treating brackish water with relatively low total dissolved solids (TDS), UF can be used both as pretreatment to a RO system and to produce permeate for blending with RO product water.

Sludge Production

In the water treatment process, by-product solids (sludge) produced by removal of contaminants from raw water become a disposal problem. To minimize costs of sludge handling, the volume of sludge produced should be reduced as much as practicable.

Reduction in the weight of solids removed from raw water is impossible of course, if quality goals are to be achieved. Any weight reduction then must come from reduction in chemicals added for coagulation and flocculation.

In addition to weight reduction, the type of sludge produced should be controlled if possible, to produce a minimum volume and to yield a compact sludge that is easy to dewater and dispose of. In general, this may be accomplished by reduction or elimination of inorganic salts that tend to produce light, fluffy sludge, not readily dewatered. To reduce sludge volume and improve sludge compactness, it is possible to partially or completely replace the metal salt by organic polymers, or replace the metal salt with newer generation hydrolyzed metal salt coagulants.

In the 1980s, new generations of inorganic metal salts called (PACl) and aluminum chlorohydrates (ACHs) emerged in the United States. ACH is a highly concentrated solution of polyaluminum hydroxychloride. ACH is characterized by having the highest aluminum concentration (23% Al_2O_3) of any commercially available aluminum-based solution. The basicity of ACH at 83% is also the highest available for any polyaluminum-based solution. Basicity refers to the degree of acid neutralization and represents a measure of the ACH aluminum polymerization. PACl are concentrated solutions of lower aluminum concentrations (5–18%) and lower basicity as compared to ACH.

The highly polymerized aluminum species in ACH have much higher cationic charges than aluminum in standard salts such as alum or aluminum chloride and even other polyaluminum products. Therefore, ACH can offer both a higher level of performance and lower overall dosages. The high degree of acid neutralization (basicity) means that the effect on pH when applying ACH is negligible. ACH effectively coagulates over a broader pH range (as high as 9.5) versus traditional metal salts and lower basicity PACl.

ACH is generally employed as the primary coagulant in potable water and industrial water treatment plants, replacing need for other coagulants such as alum, and in many cases eliminating or at least greatly reducing need for pH adjustment chemicals. ACH is often employed in an environment where pH of the receiving stream is higher than 7.5. As with other metal salts, ACH and PACl dosages may be reduced with use of organic polymers.

Sludge from precipitation softening processes usually cannot be reduced significantly in weight, since they are primarily a result of dissolved hardness precipitation rather than addition of unnecessary chemicals. Where softening is achieved by ion exchange, it is possible to reclaim salt from spent regeneration solutions, while producing solid waste consisting of calcium and magnesium salts. Recycled salt brine can then be used for subsequent regenerations.

Once water treatment chemistry has been investigated to determine the optimum process producing the least amount of by-product sludge, consideration then focuses on the type of disposal process needed to handle solids. Where applicable, potential use of by-product material by a local industry should be considered. This may include such diverse activities as brick manufacturing, wallboard production, and agriculture. The alkali value of lime sludge may be valuable to neutralize acidic wastes, such as pickle liquor in a steel mill. Finding practical uses for sludge not only reduces sludge handling cost, but also eliminates need for landfill of solid material. Many states regulate disposal of aluminum sludge in public landfills.

Disposal of sludge by retention in sludge lagoons appears, at first, to be the obvious solution to a sludge disposal problem. Unfortunately, this often is simply a delaying process. Ultimately, sludge must again be handled, if the lagoon must be reclaimed. Lagoons may provide interim storage for a dewatering system, which continuously withdraws sludge from the lagoon at a controlled rate, optimizing design of the dewatering device. This also provides a means to completely flush sedimentation basins in older plants not equipped for continuous sludge withdrawal. Where land is readily available, sludge lagoons may provide an economical method of sludge drying, providing lagoon depth is not excessive and climatic conditions are favorable.

Sand drying beds have proved acceptable for dewatering water plant sludges. In warmer climates, they may be used year-round; in cold climates, sand beds are usually used in summer to dewater sludge accumulated throughout the year. Coupled with high molecular weight flocculants, sand beds provide a practical, inexpensive method of sludge dewatering. Sand drying beds require little attention by operators and consume very little energy. Sludge harvesting methods should be considered in designing the beds, so that mechanical equipment can be used.

Dewatering by centrifugation has gained popularity because of the compact nature of the equipment, and its ability to be operated with relatively little operator attention. Special attention must be given to details of equipment design to minimize internal abrasion by grit, which leads to costly maintenance. This equipment is able to handle wide variations in feed solids without significant upsets in production. Supplemental polymers required for inorganic sludge dewatering must comply with Treatment Techniques for Acrylamide and Epichlorhydrin. Products must contain less than 0.05% residual acrylamide monomer, if centrate is reused in the drinking water process.

The plate-and-frame filter press has been successfully adapted to dewatering municipal water plant sludge. To properly assess this process, both capital and operational costs must be compared to alternative methods. In some cases, very high doses of filler such as diatomaceous earth, lime, or fly ash have been required to produce an acceptable cake. Early designs required considerable labor per unit of dry cake production, but newer designs have improved upon this.

The belt press includes several varieties of designs of screens or cloths on a conveyor device to reduce sludge volume. Often, solids are discharged as paste. In some cases, additional stages use press rolls to squeeze out more water and produce a more concentrated cake for disposal.

Filter backwash water, containing relatively little solids, requires separate treatment. In many cases, it is possible to simply pump backwash water directly to the head of the plant without upsetting the normal clarification process. However, consideration of the proliferation and concentration of *Cryptosporidium* and *Giardia* must be weighed, when water is reused in the treatment process. To facilitate this, it is desirable to add a polymer coagulant directly to the recycle stream during the time the backwash waste is being returned. This agglomerates the solids and prevents them from upsetting the clarification process. Backwash flow rate is often so high that direct return to the sedimentation basin may create a momentary overload. High flow rates can be controlled by an intermediate equalizing basin. Where sedimentation basins are not employed, use of decant tanks to concentrate the sludge, followed by sand bed dewatering, should prove adequate.

Municipal Sewage Treatment

While municipal sewage treatment is a well-established practice, it is an area of water treatment experiencing revolutionary changes because of increasingly stringent effluent quality limitations, and the potential value of treated effluent as a source of water for industry, agriculture, and municipalities. Until a few generations ago, plants were designed to remove 30 to 40% of undesirable impurities before discharge into the receiving body of water. There were no real limits on effluent quality as long as the discharge was chlorinated and met bacterial count standards. Municipal sewage plant operators had only minimal training, but fortunately, many of them were able to learn from experience and became knowledgeable in plant operations. With growing sophistication of modern plants designed to meet stringent goals, training programs in sewage plant operation have become available to supplement on-the-job training for upgrading personnel.

In the late 19th century, fewer than 30 cities had sewage treatment facilities. Today, more than 16000 municipal wastewater treatment plants operate in the United States, ranging in size from several hundred mgd to less than 1 mgd (<158 m^3/h). Roughly 1000 of these facilities operate with a total influent flow greater than 5 mgd (789 m^3/h). According to the EPA, 75% of U.S. wastewater is treated in regional collection and treatment systems.

Overview

Sewage treatment refers to the processing of primarily domestic sewage produced by typical community and household activities. In rural areas, characteristics of raw sewage tend to adhere to this definition. As cities become larger and more industrialized, waste volume and characteristics of one particular industry may affect sewage composition. In addition, sewage may be from combined or separate sanitary sewer systems.

With combined systems, storm water drains into sewer lines to become part of the total flow to the sewage treatment plant. Such uncontrolled surges in flow can be very disruptive to the process of sewage treatment, severely limiting the plant's ability to remove pollutants. Future practice aims toward segregating storm water flow in sewer systems from those used to collect sanitary waste. This will materially reduce and control flow entering the treatment plant, thereby increasing ability to maintain adequate treatment. Storm water retention basins are being built in many cities to even out severe surges caused by storm water, allowing a more reasonable chance of processing the extra volume.

The flow of sewage to be treated may approximate the flow of municipal water supplied to the same community, being in the range of about 100 gpd (0.38 m^3/day) per capita in rural areas to 150 gpd (0.57 m^3/day) per capita in urban areas with industrial users. However, there may be differences between municipal water and sewage flows that could be substantial. Such differences may be caused by evaporation losses in industrial plants (over cooling towers or as noncondensed steam), storm water or groundwater influx, and local industries that may have their own water sources but discharge into municipal sewers. Sewage is always warmer than the water source, and shows an increase in salinity over potable water of about 50 to 75 mg/L. The most common contaminant additions to filtered municipal water as it is converted to sewage are:

- Suspended solids, typically about 200 mg/L, of which about two-thirds is organic and two-thirds is settleable
- Dissolved organic matter, typically about 150 mg/L as biochemical oxygen demand (BOD)
- Nutrients, typically 10 to 30 mg/L phosphate and 10 to 30 mg/L ammonia

Standards being established for pretreatment of industrial wastes for discharge into municipal sewers are helping to reduce harmful contaminants found at lower concentrations, such as heavy metals and cyanides from plating operations, oil and grease from metalworking and food-processing plants, and toxic materials [e.g., polychlorinated biphenyls (PCB), pesticides, and solvents] as specified by the EPA.

Because sewage flow patterns are directly related to residential water use, there are wide variations in inflow during the day, the week, and even the season. Figure 44.4 indicates the degree of variation throughout the day caused by typical residential use patterns. During the week, flows vary because of other factors, such as the traditional Monday washday. Seasonal variations also affect separate sanitary sewers owing to the impact of storm water caused by damaged sewer pipe (infiltration) and sump pump operation.

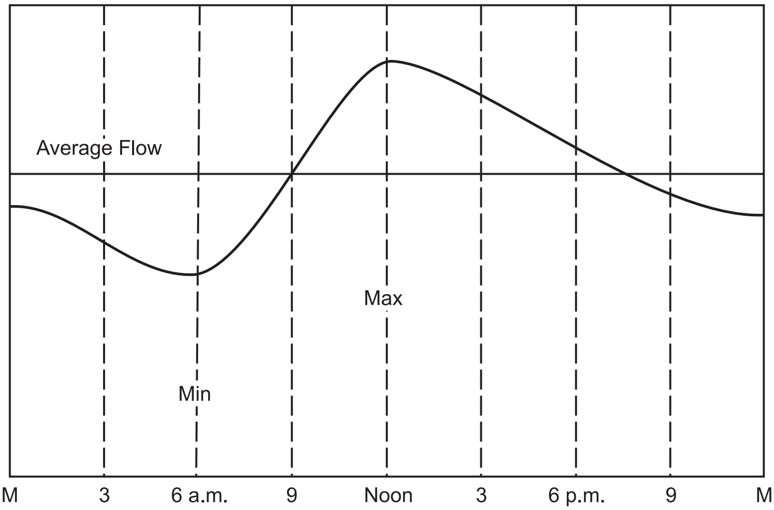

FIGURE 44.4 Typical diurnal variation in sewage flow.

While combined sewer systems are mostly influenced by sudden downpours (inflow), separate systems are affected over a broader period because of the slower drainage of water from saturated soil. After a considerable dry spell, soil acts as a sponge, reducing the impact of short infrequent showers.

Wastewater Treatment Methods

Wastewater treatment practices vary in the type of equipment used and in treatment sequences. Most plants fall into a few basic categories, as shown by the simplified flow sheets in Fig. 44.5. While these flow sheets show basic unit operations that make up the total process, they do not include supplemental treatments such as ammonia stripping or selective ion exchange. These additional processes develop from individual plant needs related to sewage characteristics and flow and effluent limitations to be met. Since the Clean Water Act requires all plants to practice secondary treatment, only those treatment schemes that include secondary treatment are shown. Stabilization ponds, which provide treatment for smaller municipalities, are omitted. Here, wastewater is contained in a pond for long periods

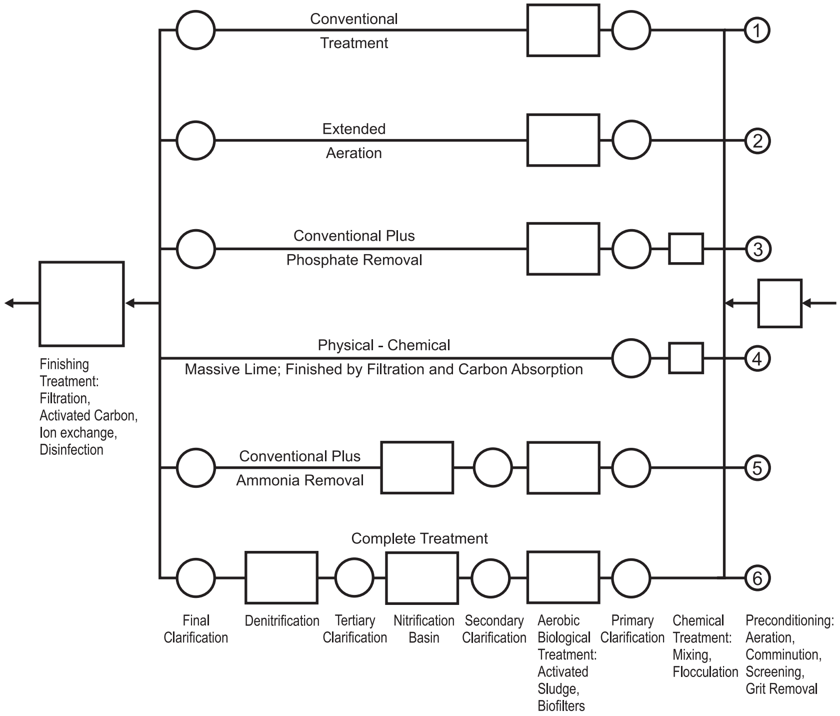

Figure 44.5 Typical processes available for municipal sewage treatment.

during which useful bacteria and algae consume undesirable pollutants. Refer to Chaps. 22 to 24 for a detailed discussion on primary, secondary, and tertiary treatment.

Disinfection

Wastewater discharged into a receiving body still contains microorganisms and pathogens that can produce disease and therefore requires disinfection. While disinfection may take various forms, chlorine application to a detention basin providing at least 15 minutes reaction time has usually been used for this purpose. In many cases, dechlorination may follow to remove trace amounts of residual chlorine that might be toxic to stream organisms. Due to hazards associated with chlorine gas, it is used less frequently then in the past. Because of concern for the production of chlorinated organics, which might also be toxic, other methods of disinfection are gaining popularity. Ozone and UV light are other disinfection techniques. Ozone, while expensive, does not leave a residual that requires further removal and is very effective at destroying viruses and bacteria. UV light also does not require further treatment for removal of residuals.

Lagoons

Since the 19th century and even earlier, wastewater lagoons or ponds have been used as a process for wastewater treatment. In the 1920s, artificial ponds were designed and constructed to receive and stabilize wastewater. By 1950, ponds had become recognized as an economical wastewater treatment method for small municipalities and industries. As of 1980, approximately 7000 waste stabilization lagoons were in use in the United States. By the 21st century, over 30% of all secondary wastewater treatment facilities in the United States with flows less than 1 mgd (<158 m^3/h) include some type of pond system. However, ponds can be used for larger cities, primarily in stable climates, for wastewater treatment as well. Some of the largest pond systems in the United States are in Northern California, serving such cities as Sunnyvale, Modesto, Napa, and Stockton.

A wastewater lagoon or pond is an engineered system designed to allow water, algae, bacteria, and oxygen to interact biologically and physically. There are several types of lagoons.

Waste stabilization ponds (WSP) are also known by the name of oxidation ponds or lagoons and decompose carbon biologically in up to three stages in series, depending on organic strength of input waste, and effluent quality objectives. Generally, WSP consist of an anaerobic pond following primary or secondary facultative ponds. If further pathogen reduction is necessary, maturation ponds are introduced to provide tertiary treatment. In WSP, bacteria and algae stabilize and reduce pathogens to convert organic content of the effluent to more stable forms. These ponds are useful in treating a variety of wastewater, from sewage to complex industrial waters. They can function well in a wide range of weather conditions and can be used either alone or integrated with other treatment processes. WSP are regarded as the method of first choice for treatment of wastewater in many parts of the world, because of design, construction, and operation simplicity, cost-effectiveness, low maintenance and energy requirements, easy upgrading, and high efficiency.

Advanced integrated wastewater pond systems (AIWPS) are feasible for application in the developing world. AIWPS designs incorporate a minimum of four low-cost ponds or earthwork reactors in series. These are advanced facultative ponds (AFP), secondary facultative ponds or algal high rate ponds (HRP), algae settling ponds (ASP), and maturation ponds. Sludge management and removal in AIWPS is minimal since sludge remains in place and biologically degrades over decades. Methane fermentation and biological assimilation transform carbon. Conversion of waste organic solids to methane, nitrogen gas, and carbon dioxide via methane fermentation, and assimilation of organic and inorganic carbon to algal biomass via photosynthesis provide the basis for primary, secondary, and tertiary treatment in AIWPS.

Water Reuse

Water reuse is becoming more prevalent in municipalities in the United States. Reuse offers a source of water that is dependable, locally controlled, generally beneficial to the environment, not affected by climatic changes, and applicable for nonpotable applications such as irrigation; toilet and urinal flushing; industrial processing; power plant cooling; wetland habitat creation, restoration, and maintenance; and groundwater recharge. Additionally, water reuse allows communities to become less dependent on finite groundwater and surface water sources. Indirect and direct potable reuse (IPR and DPR) plants are being considered in many municipalities throughout the United States. In some cases, reuse is potentially more cost-effective than seawater as a source water because of the cost of desalination.

Water reuse facilities use a variety of treatment processes to treat influent water. Generally speaking, the four stages of treatment are primary, secondary, tertiary or advanced, and disinfection. The number of treatment steps vary based on the end use for the water. The majority of recycled water is disinfected using technologies mentioned previously.

Nonpotable recycled water is distributed in a separate pipeline system to customers. Cross-connection tests ensure that nonpotable recycled water pipelines are not connected to the drinking water system.

According to the WateReuse Association, several states consider reclaimed water viable as an alternative water source, and have developed regulations with specific water quality requirements or treatment processes for a variety of reuse applications. Other states lack specific guidelines and regulations. In 2004, EPA developed a comprehensive technical document entitled Guidelines for Water Reuse, specifically as a technical resource for those states without regulations on reuse of municipal wastewater.

Denver Water Recycling Plant

Denver is a good example of a city that practices wastewater recycling and reuse for nonpotable applications. Existing wastewater plant capacity is 30 mgd (4700 m^3/h), and it is expandable to 45 mgd (7100 m^3/h). The distribution system includes over 50 miles (80 km) of pipe with two major pump stations and dedicated storage facilities. At completion, the project will supply about 17 mgd (2700 m^3/h) of treated wastewater to irrigation and industrial customers.

Wastewater Treatment Process Source water for the recycling plant comes from Metro [Denver] Wastewater's treatment plant. Figure 44.6 shows how wastewater is treated before release. Denver Water gets its share of water after the water has been fully clarified.

Wastewater from the sewer system enters the plant, where it is filtered through bar screens and grit basins, which remove large objects. During the first clarification process, solid waste settles to the bottom. Water is exposed to aerobic microorganisms in secondary treatment that digest the remaining organic waste. The secondary clarifier removes most of the suspended solids. At this point, part of the treated water is pumped to Denver Water's recycling plant. The rest of the water is chlorinated and dechlorinated. Finally, the cleansed wastewater enters the South Platte River.

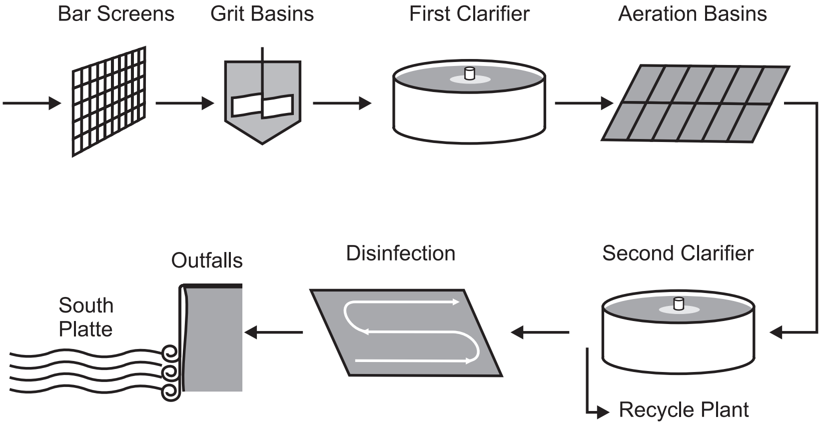

FIGURE 44.6 Metro (Denver Colorado) wastewater treatment process.

Denver Water Treatment Process The process that Denver Water uses to create recycled water is very similar to the process for creating potable water. The primary differences are the source of the water and a pretreatment (biological filter aeration) that wastewater goes through to remove ammonia not present in the normal mountain water source. Figure 44.7 shows the four main steps in preparing water for use after the special aeration. Recycled water contains somewhat higher salt and mineral content as well as other introduced elements that make it not safe to drink but acceptable for nonpotable applications.

Source water enters the plant and is rapidly mixed with coagulants that can capture floating sediment. The water is flocculated, which creates turbulence and increases contact of sediment and coagulant. This allows particles to grow bigger and heavier. Within the sedimentation basin, clumps of sediment settle. Water then passes through anthracite filter beds, trapping remaining sediment. Once fully filtered, water passes into contact basins for disinfection. Finally, water is stored in a reservoir, where it is ready for industrial and large irrigation customers.

Membrane Bioreactors

Membrane bioreactors (MBR) combine activated sludge treatment with a membrane separation process. The membrane component uses low-pressure MF or UF membranes, thereby eliminating need

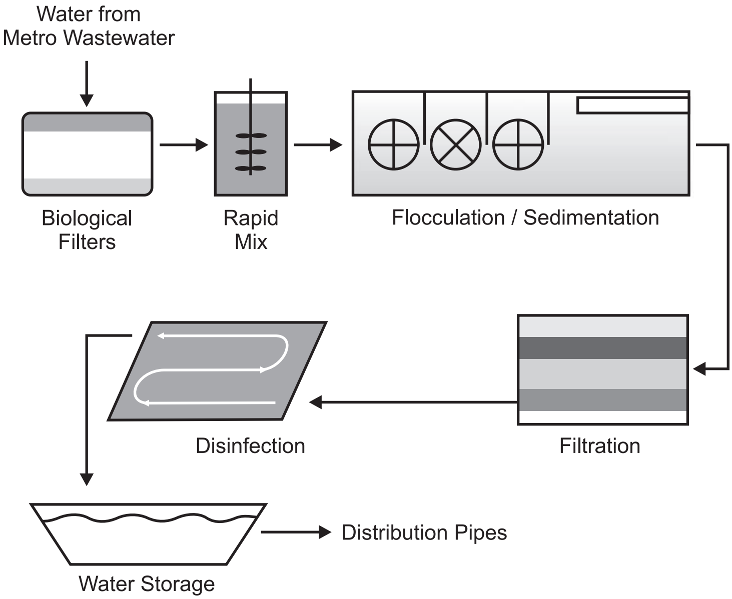

Figure 44.7 Denver Colorado water recycle water treatment process.

for clarification and tertiary filtration. Membranes are typically immersed in the aeration tank. MBR systems are differentiated in that they effectively overcome limitations associated with poor settling of solids in conventional activated sludge processes. MBR can operate higher mixed liquor suspended solids (MLSS), often in the range of 8 to 12 g/L compared to conventional systems operated in the range of 2 to 3 g/L, as the latter are limited by sludge settling. Elevated biomass concentration in MBR allows for very effective removal of both soluble and particulate biodegradable materials at higher loading rates. Thus, increased sludge retention time (SRT), usually exceeding 15 days, allows for complete nitrification regardless of ambient temperature.

In municipal wastewater applications, MBR processes are capable of producing effluent of high enough quality to be discharged to coastal, surface, or brackish waterways or to be reclaimed for urban irrigation. MBR processes typically produce water of a quality that can be used as NF or RO feed water in reuse or aquifer storage designs. Other advantages of MBR over conventional processes include small footprint, easy retrofit, and upgrade of old wastewater treatment plants. MBR are used for municipal and industrial wastewater treatment with plant sizes up to 15 mgd (2400 m^3/h).

Solid Waste Treatment

In treatment of municipal wastewater, some contaminants are actually consumed, but a significant portion simply is converted to solid wastes (biosolids). When biosolids are removed from water, they become by-product sludge, which requires disposal. The disposal of residual process solids is addressed in the Resource Conservation and Recovery Act (RCRA), which requires environmentally sensible disposal and reuse of biosolids, if possible. Over 50% of municipal biosolids in the United States are used as soil conditioners or fertilizers, and the remaining biosolids are incinerated or landfilled.

The first step in disposal of biosolids is to stabilize the sludge to eliminate odors and pathogenic organisms, as well as reduction in volatile material. Most plants use aerobic or anaerobic digesters to accomplish this. Following stabilization, sludge is concentrated and dewatered before final disposal. New processes are being continually investigated to use waste sludge. It has been used for years as a lawn and agricultural soil supplement. Sludge also finds use as fuel and as raw material for conversion to activated carbon.

Sludge is often concentrated before dewatering to permit more efficient utilization of final dewatering equipment. This is particularly true in the case of waste activated sludge, which may contain only 0.5 to 1.5% solids. Position of the sludge concentrator varies, though when used to concentrate waste activated sludge, it is generally ahead of the digester to provide a concentrated feed. In some cases, this is the final sludge processing step before landfill of digested sludge, where higher moisture does not represent significant haulage costs. Equipment used may vary greatly from plant to plant. Figure 44.8 shows a large sewage treatment plant with multiple sludge handling systems.

Many cities use incinerators to dispose of sludge generated from sewage. Additionally, many cities are considering use of biogas from anaerobic digesters as free fuel to generate electricity and power. Sometimes, sludge is combined with municipal solid waste (garbage) for incineration. Because of energy considerations, emphasis is being placed on power generation in newer units.

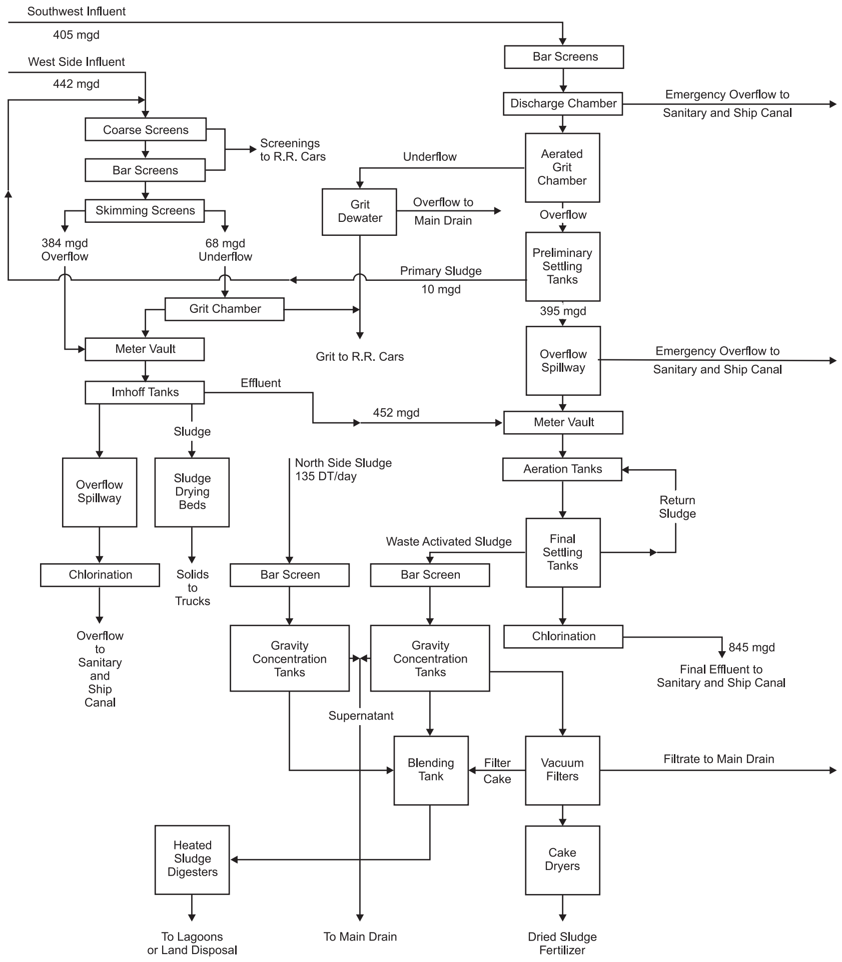

Figure 44.8 Large, complex sewage treatment plant with multiple sludge handling systems.

Dewatering

Sludge dewatering is normally the final liquid/solids separation step in a wastewater treatment process. The dewatering method is often dictated by the nature of solids being dewatered, final method of sludge disposal, and specific local conditions. The goal is to produce a dewatered sludge cake of such density, solids content, and strength to meet subsequent sludge disposal requirements. For example, maximum water needs to be extracted from sludge if it is going to be incinerated to minimize use of auxiliary fuel. Low cake moisture (high solids concentration) can be required to pass cake drainage tests for landfills and minimize hauling costs. Sludge may not need to be dewatered to such a high extent when cake is used for a land reclamation program.

Chemical conditioning is a term that denotes sludge that has been treated to decrease specific resistance and increase porosity. Chemical conditioning may include any combination of polymer addition, mixing energy, and at times dilution water. The process is designed to produce a porous, three-dimensional sludge matrix, which releases water readily during the dewatering operation. Optimum chemical conditioning increases particle size of solids, releases surface-adhering water, and decreases sludge compressibility.

The majority of municipal anaerobically digested biosolids require a cationic polymer of some form due to the natural anionic charge of biosolids.

Refer to Chap. 26 for a detailed discussion of sludge thickening and dewatering.

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