ASSOCIATION OF WATER TECHNOLOGIES

Technical Reference and Training Manual

2nd Edition

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Preface

The Association of Water Technologies (AWT) was founded in 1985 by a group of regional water treatment company owners who were concerned about the future of our industry. Since then, the growth of the Association has been unprecedented and has truly been a means of distinguishing the water treatment industry.

Contained in the Mission Statement of the Association of Water Technologies is the obligation; "AWT is dedicated to serving its member firms by providing business and professional education..." The introduction of this manual, which has been appropriately named the *Technical Reference and Training Manual*, is the culmination of many years of diligent, thoughtful work by many AWT members in an effort to fulfill the mandate of our mission statement.

At early AWT conferences, the need for a source of technical training was the subject of almost every committee meeting. In those days, the Education and Technical Committees were one and the same. It was decided that a technical reference manual should be produced as quickly as possible. A few dedicated members of that committee took this arduous and difficult task of producing a reference manual as soon as possible. A group of dedicated members of the Education and Technical Committee took individual chapters and at great personal cost, produced the first Technical Reference Manual. Since then, the Technical Reference Manual served the Membership of AWT by providing basic water treatment technology to new and fledgling newcomers to the water treatment industry. We owe a debt of gratitude to these early authors who provided an invaluable service to all our membership.

The Board of Directors, after considerable deliberation, decided the new manual should be retitled the *Technical Reference and Training Manual*. It was decided to ask a group of our very qualified consultant members to undertake this special project. The Board selected Dr. Arthur J. Freedman to be the Editor-in-Chief for the project. Although Dr. Freedman was selected as the Editor-in-Chief, a different writer authored each chapter. This edition of the *Technical Reference and Training Manual* contains the first four chapters, which are:

1. Basic Water Chemistry	Dr. Arthur J. Freedman
2. Pretreatment	Irvin Cotton
3. Boiler Water Treatment	Dr. Orin Hollander
4. Cooling Water Treatment	Dr. Bennett P. Boffardi

This manual has been designed with a dual purpose in mind.

a) Provide a resource to the water treatment field person who would like to have a reference in the field that can be referred to as needed.
b) To be used as a curriculum to train new water treatment professionals.

This manual must be viewed as a work in progress. Additional chapters will be added to provide reference and training in important future developing areas of water treatment technology and chemistry. Once in the hands of eager students and skillful trainers, this manual will provide a firm foundation for planning, implementing and controlling successful water treatment program.

In addition to these authors, a special thanks should go to the members of the Technical Committee who have spent countless hours reviewing this material in the manual. A special thank you to the staff of AWT, specifically Elise Lindsey, Executive Director and Carrie Harley, for their dedication to this project.

Although all of those listed above have supplied an invaluable contribution to this manual, a special expression of gratitude should go to the total membership of AWT, who have provided encouragement to the Board of Directors to see that this project is completed.

Alfred J. Nickels
President 2000
Association of Water Technologies

Preface to the Second Edition

This second edition of the Association of Water Technologies (AWT) *Technical Reference and Training Manual* continues the tradition of the first edition. That is, to serve as a basic training guide and also as a reference source of advanced water treatment information. The Manual should be useful to water treatment professionals at all levels, and also to end users who wish to improve their understanding of water chemistry and water treatment technology.

Chapters 1 through 4, covering water chemistry and boiler and cooling water technology, have been revised and updated. Technical and editorial errors have been corrected, and more information has been added concerning advanced water treatment technologies that are becoming widely used. The second edition also includes chapters on wastewater treatment, regulatory compliance in the water treatment industry and potable water.

The authors have made valiant efforts to find and correct errors. This is an ongoing and seemingly never-ending search. We thank Heidi Zimmerman, Executive Director, and the AWT staff for their help in this process, and in formatting and publishing the Manual. We ask our readers to inform the AWT office of any further errors that may be discovered.

Finally, as with the first edition, we gratefully acknowledge the continuing support of the AWT Board of Directors and Technical Committee, which have made this second edition of the *Technical Reference and Training Manual* possible.

Arthur J. Freedman, Ph.D.
Editor

Author Biographies

Dr. Arthur J. Freedman, Ph.D. – Author, Introduction and Chapter 1, and General Editor

Dr. Arthur J. Freedman has been working in the water treatment field for forty-two years. He received his Ph.D. degree in inorganic chemistry from New York University in 1948. He worked in radiochemistry at the Massachusetts Institute of Technology, the Los Alamos Scientific Laboratory and the University of New Mexico. He then joined Amoco Oil Company, where he became involved in corrosion problems. In 1959, Dr. Freedman joined Nalco Chemical Company, where he worked for twenty-two years as Technical Director and Marketing Manger in cooling water, boiler water and wastewater treatment. Dr. Freedman retired from Nalco in 1981 and formed his own consulting company, Arthur Freedman Associates, Inc.

Dr. Freedman holds five patents and has written well over fifty publications covering various aspects of water treatment. He has contributed to several well-known textbooks and compendia of papers, edited books and manuals, and written training manuals for large corporate users of water treatment. He is a member of the editorial advisory board for *Materials Performance.*

Dr. Freedman is a fifty-year member of the American Chemical Society (ACS), and actively participates in the International Water Conference (IWC), NACE International (NACE) and the Association of Water Technologies (AWT). Dr. Freedman has presented numerous papers, chaired committees and symposia, and served as Chair of the NACE general committee on Corrosion by Water. He received a Distinguished Service Award from NACE International in 1999, and in 2000, AWT honored Dr. Freedman with the Ray Baum Award for service to the water treatment industry.

Dr. Arthur J. Freedman

Irvin J. Cotton – Author, Chapter 2

Mr. Irvin J. Cotton is a principal consultant with Arthur Freedman Associates, Inc., specializing in external treatment, boiler water, cooling water, process water and wastewater systems. His experience includes system performance reviews, problem solving, failure analyses, continuing surveillance and system audits. Clients include water treatment industry companies as well as end users in large and small industrial plants, commercial buildings and utility stations. Mr. Cotton has been providing water treatment consulting services for 33 years.

Mr. Cotton graduated from the University of Cincinnati in 1964 with a B.S. degree in chemical engineering. Following service in the Armed Forces as a Lieutenant based in the U.S. and overseas, he was employed by 3M Corporation as a Process Engineer responsible for manufacturing processes. In 1998, Mr. Cotton retired from BetzDearborn Corporation after 30 years, where he served at various times as Engineering Consultant for all industries, Product Manager for boiler water treatment chemicals, and Technical and Marketing Manager for Boiler, Cooling and Wastewater chemicals for the Refining and Petrochemical Industries.

Mr. Cotton's professional activities include membership on the Editorial Advisory Board for *Materials Performance*. He is a member of the American Society of Mechanical Engineers (ASME) and NACE International (NACE), where he has served as Chair of various technical committees. He is also a member of the American Society for Testing Materials (ASTM) and the American Institute of Chemical Engineers (AIChE). He has over 40 publications in all areas of water technology and treatment.

Mr. Irvin J. Cotton

Dr. Orin Hollander, Ph.D. – Author, Chapter 3

Dr. Orin Hollander is President of Holland Technologies, Inc. He holds a B. A. degree in chemistry from Northwestern University, and a Ph. D. in inorganic chemistry from Ohio State University. Dr. Hollander has twenty-one years experience in water treatment technology for industrial systems, including seventeen years at BetzDearborn Inc. His work includes basic and applied research into corrosion and corrosion inhibition in cooling water and boiler water, and in pretreatment systems. He also spent eight years in technical marketing in the power industry. In 1996, Dr. Hollander organized Holland Technologies, Inc., where he serves as President, specializing in consulting services for industrial water treatment.

Dr. Hollander's previous experience at Engelhard Industries includes 5 years R&D in pigments and fillers, and catalyst support media.

Dr. Hollander is a member of the American Chemical Society (ACS), NACE International (NACE) (T7-1 Chairman), the Technical Association of the Pulp and Paper Industry (TAPPI), and the Association of Water Technologies (AWT) (Boiler Technical Committee Chairman). He has authored numerous technical publications and is a member of the editorial advisory board for *Materials Performance*.

Dr. Orin Hollander

Dr. Bennett P. Boffardi – Author, Chapter 4, Chapter 7

Dr. Bennett P. Boffardi is president of Boffardi & Associates, Inc., a firm specializing in water treatment consulting. He is an internationally recognized expert in corrosion inhibition and scale & deposit control in aqueous systems. During his career in research & development and technical service at Calgon Corporation, he developed new chemical treatment programs and computer simulations of cooling water systems.

Dr. Boffardi holds 17 United States patents covering the control of corrosion and scale in water applications. He has published 55 technical articles and authored 3 books. He has received numerous national, corporate and technical awards, including being honored as a fellow by NACE International (NACE).

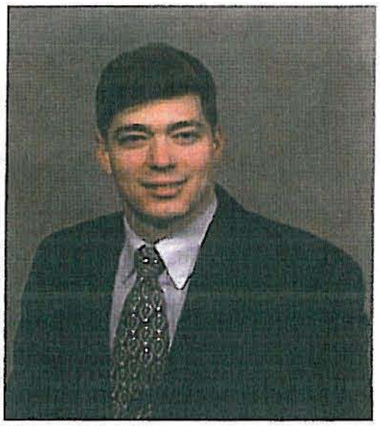
Dr. Boffardi's active role in NACE spans four decades and includes serving on seven committees at the national level, in addition to serving as a National Director and as a National Member-at-Large. Dr. Boffardi is also a member of the American Chemical Society (ACS), the American Water Works Association (AWWA) and the Association of Water Technologies (AWT). He is currently Technical Editor of AWT's quarterly magazine, *The Analyst*.

Dr. Boffardi holds a Bachelor's degree from St. John's University and a Master's degree from the Polytechnic Institute of Brooklyn. He returned to St. John's where he earned his doctoral degree in chemistry.

Dr. Bennett P. Boffardi

John G. Krenson – Author, Chapter 5

Mr. John G. Krenson, a principal of Besway Systems, Inc., has spent over twelve years in the manufacturing of chemical products including water treatment products. His expertise includes formulating and manufacturing operations. Mr. Krenson has unique expertise in regulatory compliance and safety training for OSHA, EPA, and DOT standards at the federal, state, and local levels. He has assisted a wide variety of manufacturers, distributors, service consultants and end-users in developing their own compliance programs. He has also trained hundreds of people – from business owners to on-the-floor production personnel – on safety and compliance issues. His clients have included sole proprietors and Fortune 500 companies. He has survived and has helped others survive several OSHA, EPA, and DOT audits. Mr. Krenson has authored several regulatory reference manuals, articles, testified before OSHA committees, and has negotiated penalty reductions for clients. John has been associated with AWT for over six years. He was educated at Marquette University in Milwaukee, WI. He resides in Nashville, TN with his lovely wife Carrie and their daughter Daria.


John G. Krenson

Section 2.3 in Chapter 5, covering FIFRA, was contributed by Ms. Joan Young, formerly Chief of Regulatory Affairs at Union Carbide Corporation."

AWT Wastewater & Pretreatment Committee – Authors, Chapter 6

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(i) INTRODUCTION

An Overview of Water Treatment

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INTRODUCTION

An Overview of Water Treatment

1.0 Overview

1.1 OBJECTIVES OF THIS MANUAL

This manual is a sourcebook of technical information for water treatment professionals. It contains information on the properties of water that affect the way water is used in commercial buildings and industrial plants. These same properties create the problems that water treatment professionals must solve when designing and servicing water treatment programs for specific applications.

This manual is intended to be used. Do not let it gather dust on the shelf. Study it to learn the basic technology of the water treatment industry. Use it to help explain problems that arise in the field. Use information from this book in discussions with customers, to help them understand the technology of water treatment.

In addition to water treatment technology, it is important to understand the basic technology of customer plants. Chemical and manufacturing process operations are not discussed in this manual. Many good reference books cover these subjects. Some are listed at the end of this introduction.

This manual is both a technical reference and a training and education tool. For that purpose, the manual includes technical references and articles for further study. Also, review questions at the end of each chapter help the reader to test his/her knowledge to be sure that important information is properly understood.

1.2 OBJECTIVES OF WATER TREATMENT

The function of industrial and commercial nonpotable water systems is to add heat to, or remove heat from, industrial processes and commercial data centers, to generate electric power, and to condition the air in commercial buildings, hospitals, etc.

From this point of view, open and closed cooling and heating systems, and steam generation systems, are all aspects of the same general process. The objectives are to transfer heat from one place to another, using water as the transfer medium, to conserve heat energy, and to discharge waste heat and water to the environment in an acceptable way.

Thus, the general objectives of water treatment must be:

a. To keep heat transfer equipment as clean as possible, in order to maximize water flow and heat transfer efficiency.

b. To protect the heat transfer equipment and associated piping from corrosion and fouling damage.

c. To conserve water and heat, and to meet or surpass all applicable air and water quality regulations.

d. To accomplish all of this in the most technically appropriate, safe and cost-effective way possible, in the best interests of the customer.

These objectives are interrelated and should be considered together as general guidelines for planning comprehensive water treatment programs for industrial and commercial facilities.

1.3 COMMERCIAL AND INDUSTRIAL WATER SYSTEMS

Because of its general availability and low cost, water is the world's most widely used heat transfer medium. Following is a brief description of the major systems that water treatment professionals encounter in commercial buildings and industrial plants. All of these systems are explained in detail in chapters 2, 3 and 4 in this manual.

1.3.1 Cooling Systems

Cooling water systems are defined as either "closed" or "open". A closed loop system is intended to be sealed, requiring makeup only to replace water lost by leakage, construction, etc. An open system, on the other hand, is in contact with the atmosphere and is cooled by evaporation in a cooling tower or spray pond. Water lost by evaporation is replaced by makeup water, and a fraction of the circulating water is removed continuously to maintain water quality.

Heating, ventilating and air conditioning (HVAC) systems are used to condition the air in commercial buildings and industrial sites. A typical HVAC cooling system includes both a closed and an open cooling water circuit. First, chilled water circulating in a closed loop absorbs heat from building air in large air handling units and fan coils. The warmed water is cooled in a refrigeration machine, or "chiller", by heat exchange with a refrigeration fluid such as "Freon". Other types of chillers are also used. Then, the heated refrigeration fluid is cooled by heat exchange with an open circulating cooling water system that transfers heat to the atmosphere.

Open and closed cooling water systems are also required to cool industrial processes such as reaction kettles, furnace hoods and doors, engine jackets, and large steam condensers in electric generating plants. System sizes for both open and closed cooling systems range from a few hundred gallons to several million gallons. All of this water requires chemical treatment to protect the heat exchangers and piping, and to maintain operating efficiency.

Power stations and industrial plants situated on lakes and rivers often use once-through cooling systems. Water is pumped from the source directly through steam condensers, for example, and back to the source. Some large commercial buildings also use once-through cooling water. Many once-through systems have been converted to recirculating systems to conserve water and to protect the quality of natural water sources.

1.3.2 Heating and Steam Generating Systems

Steam and hot water systems can be classified into three groups:

a. Steam and hot water for space heating and humidity control In commercial and residential HVAC systems, and industrial plants.

b. Steam for industrial process heating and for use as a process reactant in chemical plants, paper mills, etc.

c. Steam to drive turbines for electric power generation.

Hot water heating systems are similar to closed cooling loops, but the process is reversed. The hot water adds heat to an HVAC system, or to an industrial process. The hot water temperature is maintained either by heat exchange with a steam source or by direct firing in a hot water heating boiler. This is a misnomer, since no boiling occurs, but these units are similar in appearance to small steam generators.

Steam generators range from small heating boilers to very large and complex systems generating steam for industrial plants and electric utility stations. As with cooling systems, all boilers operate on the same basic principles. Water is heated in a carefully designed system to produce steam at the desired temperature and pressure. The steam does work, by driving a turbine, heating a building or an industrial process, or becoming a reactant in a chemical process. To conserve water and energy, waste steam is condensed after use and a portion of the condensate is returned to the boiler as feedwater, along with required fresh makeup water. All parts of this system, including feedwater preparation, the boiler and the condensate system, require chemical treatment to protect the equipment, maintain boiler efficiency and prepare steam with the required quality and purity.

1.4 THE WATER TREATMENT BUSINESS

Thus, the business of water treatment consists of modifying existing water supplies to make them suitable for specific intended uses as described above.

This general process consists of three parts:

a. External treatment, also called pretreatment, before the water is used.

b. Internal treatment of boiler and cooling water while the water is in use;

c. Waste water treatment to make water removed from the system suitable for discharge or reuse.

The specific technologies used in these water treatment processes are the subject of this technical manual.

Chapter 1 in this manual explains basic water chemistry, problems that develop when water is used for cooling and heating purposes, and the use of water treatment to help solve these problems. The information in this chapter is very important. It is fundamental to understanding all of the more detailed water treatment information in later chapters.

Chapter 2 covers external treatment. External treatment of water may involve chemical and physical processes such as:

a. Settling and filtration to remove suspended solids.

b. Softening, ion exchange and reverse osmosis to reduce or remove dissolved solids.

c. Deaeration to remove dissolved gases from boiler feedwater.

Chemicals are often added to physical processes such as settling and filtration, to improve performance.

Chapters 3 and 4 cover the internal chemical treatment of boiler and cooling water. Internal treatment includes the use of chemicals to control corrosion, mineral scaling, general deposition and microbiological fouling problems, and to improve operating efficiency.

Similarly, chapter 5 describes the chemical treatment of potable water.

Wastewater treatment (Chapter 6) includes primary physical treatment, such as settling; secondary microbiological wastewater treatment such as in activated sludge plants and trickling filters; and tertiary chemical treatment, such as with activated carbon, to remove remaining objectionable soluble materials in the water.

Finally, chapter 7 covers health and safety issues that are important for every water treatment professional and for his/her customers.

2.0 Attributes of Water

Water is a unique substance. It is the world's most plentiful liquid, but it is not evenly distributed. Water quantity, quality and purity vary widely. In many cases, the most readily available water sources are also the least useful.

The selection of water supplies and treatment methods is therefore a site-specific process. It depends on both the intended uses of the water and the availability and quality of the local water supplies. To help put these supply and selection problems into perspective, it is helpful to understand some of the important and useful properties of water.

2.1 AVAILABILITY AND DISTRIBUTION OF WATER

There is plenty of water available. For example:

a. The entire world land mass will fit into the Pacific Ocean, with room to spare.

b. The world's supply of ground water, if brought to the surface, would cover all land masses to a depth of about 3000 feet.

However, the distribution of this water is poor and the quality varies widely:

a. Sea water, which can be used as cooling water and can be desalinated for use as boiler feedwater and potable water, is only available in the coastal areas of the United States. Brackish well water can also be treated this way.

b. New Orleans, LA receives too much water, over 60 inches of rain per year, and must protect itself against flooding.

c. Portland, OR receives about 40 inches of rain per year.

d. Los Angeles, CA, with a large and growing population, receives only about 10 inches of rain per year and must import water from the Colorado River and from Northern California.

e. The State of Nevada has little available and useful surface water, but it has a good supply of subsurface well water.

Obviously, as pointed out earlier in this Introduction, the most available water supply is often the least useful. Thus, considerable effort and expense may be necessary to improve the quality of brackish well water in South Dakota, or a muddy river water in Louisiana.

2.2 WATER QUALITY AND WATER PURITY

Quality and purity are not synonymous terms. It is important to understand the difference:

2.2.1 Water Quality

Water quality is an application parameter. Water quality is a measure of suitability for use in specific applications. The available water quality and the intended use will govern the type of water treatment that is required. For example, surface water that can be used directly as cooling water makeup might require substantial pretreatment for use as boiler feedwater.

Consider the three common water supplies listed in Table i-1.

a. New York City water is very soft (low calcium). It can be used directly as cooling tower makeup water. This water is corrosive, so that internal chemical treatment for corrosion control is required.

b. Chicago water contains a medium level of calcium. This water also can be used directly as cooling tower makeup, but the circulating tower water must be treated for both corrosion and calcium carbonate scale control.

c. Los Angeles (Colorado River) water is very hard (high level of calcium). If a cooling tower using this water as makeup is to be run above about 3-4 cycles of concentration, the makeup water should be softened to remove calcium hardness.

Table i-1
Comparison of Common Makeup Water Supplies
Values in mg/L except pH

Parameter	As	New York Catskill Reservoir	Chicago Lake Michigan	Los Angeles Colorado River
M alkalinity	$CaCO_3$	8.0	113	120
pH	pH	6.9	8.2	8.4
Calcium	$CaCO_3$	12.0	80.0	198
Sodium	Na	1.8	8.7	101
Chloride	Cl	2.8	6.4	71
Sulfate	SO4	11.0	17.0	290

Thus, when planning a water treatment program, it is very important to understand both the quality of the available makeup water and the available choices for operating the facility cooling towers and boilers. Water chemistry, cooling tower and boiler operations, chemical treatment and interpretation of water analyses are all explained in subsequent chapters in this manual.

2.2.2 Water Purity

In contrast to quality, water purity is a technical term. Purity is a measure of the amount of dissolved and suspended impurities in the water. Thus, by this definition, anything except H_2O molecules is, in fact, an impurity in water.

Many of the materials found in every day life are actually pure chemicals. Table i-2 lists the accepted purities of some well known materials:

Table i-2
Purities of Some Household Chemicals

Chemical	Percent Purity	Impurities, mg/L
Baking soda (USP sodium bicarbonate)	>99.95%	500
Refined white sugar	99.9	1,000
Ivory soap	99.44	5,600
Low carbon steel	99	10,000
Table salt (Iodized sodium chloride)	98.95	10,500

Water is also, in most cases, a very pure material. Consider the purities of several well known water supplies, as shown in Table i-3:

Table i-3
Purities of Some Common Water Supplies

Chemicals	Percent Purity	Impurities, mg/L
Catskill Mountains (New York City)	99.997%	30
Lake Michigan (Chicago)	99.983	170
Mississippi River (New Orleans)	99.967	330
Colorado River (Los Angeles)	99.934	660
Clean ocean water	96.5	35,000

It is surprising to most people to learn that except for ocean water, with about 3.5 percent dissolved solids, the water sources shown above are all purer than common white table sugar. In fact, Catskill Mountain water, Lake Michigan and the Mississippi River are all purer than USP baking soda!

2.2.3 Types of Impurities in Water

Even tiny amounts of impurities have remarkable effects on the properties of water supplies. Trace amounts of impurities can drastically alter the properties of water, requiring extensive physical and chemical treatment to improve water quality for specific applications.

Impurities fall into two groups:

a. Naturally-occurring impurities are leached from rocks, soil and plant life, and absorbed from the air. Most of the impurities in water are naturally-occurring inorganic dissolved solids and gases.

b. Man-made impurities include a wide variety of non-natural solids, liquids and gases, mostly the result of agricultural runoff, storm water drainage and municipal and industrial pollution.

Table i-4 lists common natural and man-made impurities in water and some of the problems these impurities can cause.

Table i-4
Impurities and Problems in Water Supplies

Impurities	Problems
Dissolved solids	
Chloride, sulfate	Corrosion, mineral scale
Calcium, magnesium, silica	Mineral scale, loss of flow and heat transfer
Phosphates	Phosphate scale, biofouling
Iron	Deposits, under-deposit corrosion
Organic matter	Corrosion, biofouling
Dissolved gases	
Oxygen	Corrosion, biofouling
Carbon dioxide	Corrosion, carbonate scale
Sulfur dioxide	Corrosion
Hydrogen sulfide	Corrosion
Suspended matter	
Silt and clay	System deposits, corrosion
Microbiological matter	Deposits, corrosion, loss of flow and heat transfer

The chapters in this manual are concerned with physical processes and chemical treatment programs used to remove these impurities from water, neutralize their effects, or in some cases take advantage of their properties for improved water treatment results.

CHAPTER 1

General Water Treatment Knowledge

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CHAPTER 1

General Water Treatment Knowledge

1.0 Overview

As explained in the Introduction to this Manual, the functions of industrial and commercial water systems are to add heat to, or remove heat from, industrial processes and commercial data centers, and to condition the air in commercial buildings. With this in mind, the two major objectives of industrial and commercial water treatment must be:

a. To keep heat transfer surfaces as clean as possible in order to maximize water flow and heat transfer efficiency; and

b. To protect the heat transfer equipment and associated piping from corrosion and fouling damage.

These two objectives are interrelated and must be considered together. This chapter therefore begins with a general discussion of the heat transfer processes and equipment that are the main business of water treatment.

Selecting, applying and maintaining optimum water treatment programs in a wide variety of applications and with many different available water sources is a complex process, To do this job well, it is important that water treatment professionals have a basic knowledge of chemical reactions in water and understand the corrosion, scaling and fouling processes that create problems requiring water treatment.

The information in this chapter provides an introduction to these subjects. College level inorganic and physical chemistry textbooks contain a more detailed discussion of heat transfer processes and water chemistry. References at the end of the chapter provide sources for further reading.

2.0 Principles of Heat Transfer

2.1 INTRODUCTION

Wherever heat is used or generated – in large and small comfort cooling (HVAC) systems, in data processing operations, in the refining and petrochemical process industries, and in industrial and electric utility power stations – heat exchangers and condensers are used for space heating and cooling and to control equipment and process operating temperatures. A condenser is simply a special case of a heat exchanger in which the process side fluid "condenses" – that is, changes phase from a gas to a liquid – by giving up heat to the cooling water flowing through the condenser tubes.

Long term stable operation of heat exchange equipment is vital for successful facility operations. The degree to which a heat exchanger approaches its design capacity may control the throughput of a large production unit, the megawatt output of a power station or the cooling that can be achieved in a high-rise commercial building.

Many factors influence the performance of heat exchangers and condensers. Some of these, such as design, metallurgy, weather conditions and product or steam demand, are not controllable. Others, such as operating modes and water treatment procedures, can be controlled by operating personnel. These controllable factors influence, to a large extent, the amount of fouling that occurs on both the process and water sides of a heat exchanger during normal operations.

Fouling, in this context, is defined as deposition of any kind, on either the process or the water side of the exchanger, that reduces heat transfer and thereby reduces the production capacity of the unit.

2.2 THE HEAT TRANSFER PROCESS

Heat can be transferred from one fluid to another either directly or indirectly. Direct heat transfer occurs, for example, when steam injected into a deaerator heats the water as it strips out dissolved gases. Deaerators are discussed in chapters 2 and 3. Indirect heat transfer occurs across an interface, usually a metal that separates two fluids but allows heat to transfer across the barrier.

2.2.1 Thermal Conductivity of Metals

Metals used in heat exchange equipment are chosen based on four factors: mechanical properties such as strength and ductility; corrosion resistance, considering both sides of the heat transfer process; material cost; and thermal conductivity. The thermal conductivities of common metals vary widely, as shown in Table 1-1. Copper, with roughly eight times the thermal conductivity of carbon steel and good corrosion resistance in water, is almost the universal choice for condenser tubing in HVAC equipment. Admiralty brass provides improved corrosion resistance and mechanical strength in some applications.

TABLE 1-1
Thermal Conductivities of Metals

Metal	Thermal conductivity BTU/hr ft. °F
Copper	411
Aluminum	164
Admiralty brass	126
Carbon steel	56
Stainless steel	19

Aluminum is used because of its light weight and good thermal conductivity, but it has less mechanical strength than other alloys and can be used in water only in the neutral pH range. Carbon steel, in spite of its relatively poor thermal conductivity, is widely used for heat transfer tubing in process applications because of its low cost relative to other alloys. Stainless steel, with the lowest thermal conductivity of the alloys in Table 1-1, is used in corrosive environments, and where long life and good mechanical strength are important. Because of its corrosion resistance and strength, stainless steel tubing can often be made with thinner walls, thus partly compensating for the poor thermal conductivity. Materials of construction in water systems are discussed in more detail in chapter 4.

2.2.2 Specific Heat of Liquids

Another important factor in the design and operation of heat exchange equipment is the heat capacity of the heat transfer fluid – that is, the ability of the fluid to absorb heat from the process side of the heat exchanger. The heat capacity of a substance is defined as the amount of heat required to increase the temperature of a substance by 1 degree. It is usually measured in units of calories per degree Centigrade. Thus, 1 calorie will raise 1 gram of water 1 degree Centigrade. Similarly, in British units, 1 BTU will raise 1 pound of water 1 degree Fahrenheit.

The term specific heat is used to compare the heat transfer capabilities of different fluids. Specific heat is defined as the ratio of the heat capacity of a fluid to the heat capacity of water at the same temperature. Table 1-2 lists specific heats for some heat transfer fluids often used in commercial and industrial processes.

In the normal temperature range of water treatment processes, the specific heat of water is assumed to be 1. Water is the "king" of heat transfer fluids. As Table 1-2 shows, no other available and practical fluid has a heat capacity even close to that of water. Fortunately for the world-wide economic system, water is also the most readily available and least expensive of all fluids.

TABLE 1-2
Specific Heats of Heat Transfer Fluids

Heat Transfer Fluid	Specific heat
Water	1.0
Ethylene glycol/water antifreeze mixtures	0.6 – 0.8
"Dowtherm A" high temperature heat transfer fluid	0.4
Liquid sodium, used in some nuclear power systems	0.3

2.2.3 Heat Transfer Across Interfaces

In a heat exchanger, the metal barrier (condenser tube, flat plate, etc.) that serves as the interface between the two heat transfer fluids develops a protective and insulating film on each surface. Considering the water side interface first, this film consists of two parts:

- Protective metal oxides, plus a layer of essentially stagnant adsorbed water molecules, next to the flowing water.
- Materials adsorbed or deposited from the water. These can include mineral scales, corrosion products, microbiological matter and miscellaneous dirt.

The metal surface next to the fluid will develop a similar film, again consisting of metal oxides, stagnant process fluid, and in some cases corrosion products and debris. Each of these layers creates resistance to heat transfer across the interface. Additional resistance occurs across the metal surface itself in contact with each fluid.

Thus, heat transfer across an interface occurs in a series of discrete steps, each of which involves a temperature drop. The term resistivity, the reciprocal of thermal conductivity, is used to describe the resistance to heat transfer that occurs at each step in this process. Heat transfer design engineers use complex formulas to calculate the resistivity at each step in determining the optimum size and configuration of the heat exchanger.

2.2.4 Monitoring Heat Transfer Efficiency

The same equations used to design heat exchangers could, theoretically, be used to monitor heat exchanger performance compared to design specifications. This, however, is neither necessary or desirable. It is difficult to obtain the data needed for these precise calculations. Also, since conditions in operating process units generally fluctuate around an average steady state, design-type calculations would lose considerable precision.

Instead, engineers calculate an overall heat transfer coefficient, U, as a measure of the overall heat exchange that occurs between two fluids in a heat exchanger. The calculated value of U includes all the losses that occur during the heat transfer process. U is defined in terms of the overall heat rate and temperature change across a heat exchanger:

$$q = UA\Delta T \qquad (1\text{-}1)$$

where q = the heat rate, in BTU/hour,
A = the heat transfer surface area, in square feet,
ΔT = the overall temperature change across the heat exchanger, and
U = the overall heat transfer coefficient, in BTU/hour ft^2 °F.

The heat rate, q, can be measured in terms of the mass flow rate of the fluids in the heat exchanger, the specific heats, and the temperature differences on either the water or the process side of the heat exchanger. The calculation is usually done with water side data, because process side flow rates are often difficult to measure. Thus:

$$q = m_w(T_{wo} - T_{wi}) \qquad (1\text{-}2)$$

where m_w = mass flow of water, in pounds per hour,
T_{wo} = water outlet temperature, in degrees F, and
T_{wi} = water inlet temperature, in degrees F.

From equations (1-1) and (1-2) it follows that:

$$UA\Delta T = m_w(T_{wo} - T_{wi}) \qquad (1\text{-}3)$$

It then remains to define ΔT. ΔT is not simply the difference between the waterside inlet and outlet temperatures. ΔT is actually the mean temperature change across the heat exchanger, considering the individual temperature changes in each field. This, in turn, is defined as the log mean temperature difference, or LMTD. The LMTD is a complex function that depends on the mode of operation of the heat exchanger. For countercurrent flow:

$$LMTD = \{(T_{pi}-T_{wo}) - (T_{po}-T_{wi})\}/\ln\{(T_{pi}-T_{wo})/(T_{po}-T_{wi})\} \qquad (1\text{-}4)$$

Where T_{pi} and T_{po} are the process side inlet and outlet temperatures.

Finally, making the substitution of LMTD for ΔT:

$$UA(LMTD) = m_w(T_{wo} - T_{wi}) \qquad (1\text{-}5)$$

These frightening equations are not as bad as they seem, because all the calculations can be done easily with the aid of simple, readily available spreadsheet computer programs.

In deriving these equations, two important assumptions were made: 1) that the specific heats of the two fluids do not vary with temperature, and 2) that all of the individual resistivity factors are constant throughout the exchanger. Neither of these assumptions is correct, but for empirical use in evaluating heat exchanger performance over time, the equations are entirely satisfactory.

Practical applications of these heat transfer equations can provide information on boiler tube temperatures and fuel usage, fouling factors in condensers, and other very important information related to equipment life and operating efficiency. These subjects are discussed in detail, with practical sample calculations, in chapters 3 and 4 in this manual.

2.2.5 Steam Condensers

These calculation methods apply generally to any operating heat exchange system. For steam condensers, the calculations can be simplified, because when steam condenses, it remains at nearly constant temperature, so that $T_{pi} = T_{po}$. Equation (1-4) then simplifies to:

$$\text{LMTD (steam condenser)} = (T_{wi}-T_{wo})/\ln\{(T_c-T_{wo})/(T_c-T_{wi})\} \qquad (1\text{-}6)$$

Where T_c = the condensate temperature.

2.2.6 Fouling Factors

Fouling in an operating heat exchanger is usually recognized in terms of less efficient product cooling leading to reduced production, increased cooling water flow required to maintain process temperatures, increased back pressure in a steam condenser, or head pressure problems in an HVAC chiller. Heat transfer performance decreases over time as deposits and corrosion products form on the water side (and sometimes on the process side) of the heat transfer surfaces.

This loss in performance is usually represented in terms of a fouling factor, R_f. R_f is the reciprocal of the overall heat transfer coefficient, U, so that the units of R_f are: hr ft_2 °F/BTU.

Design engineers usually include a nominal fouling factor when sizing new heat exchangers. That is, they size the unit to allow some fouling to occur without degrading design performance. This means that new heat exchangers and condensers are often oversized, so that cooling water flow must be throttled to control process temperatures. This, in turn, reduces the water flow rate and encourages deposition in the exchanger (see chapter 4).

Fouling factors are calculated by measuring U values for clean and dirty conditions in the heat exchanger. R_f is then calculated as:

$$R_f = 1/U_{dirty} - 1/U_{clean} \qquad (1\text{-}7)$$

U_{clean} can be calculated from design data or from operating data at the beginning of a run, after the exchanger has been cleaned. Figure 1-1 is a typical computer-generated graph of fouling factors from a pilot unit connected to a large steam condenser. Small temperature variations and electrical signals create the "noise" in this graph, but the average fouling factor is clearly close to zero and well below the upper control limit.

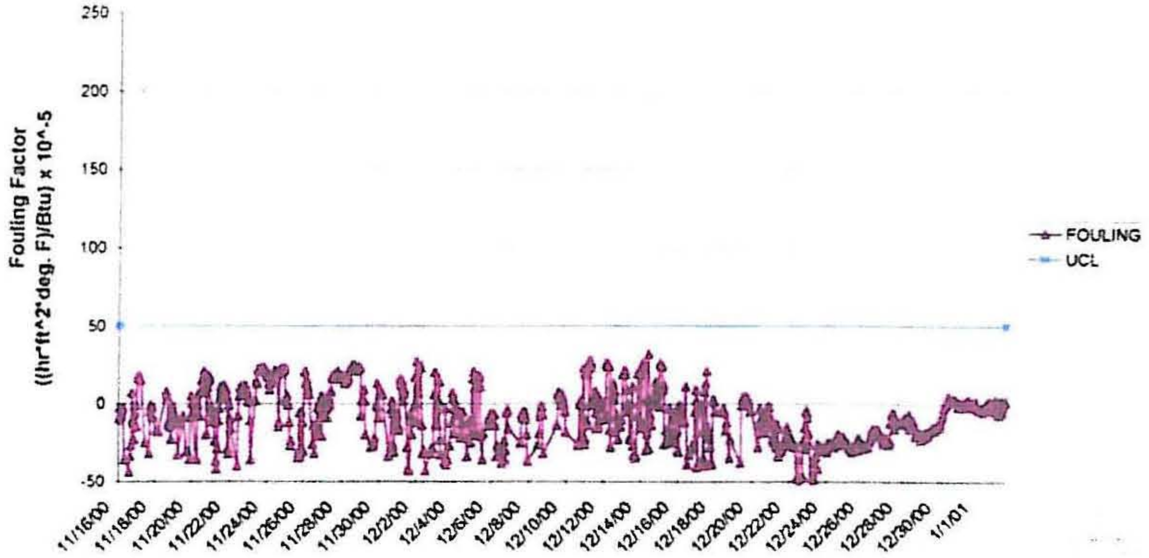


Figure 1-1. Pilot test heat exchanger fouling factors

2.3 HEAT EXCHANGE EQUIPMENT

2.3.1 Shell and Tube Heat Exchangers and Condensers

Shell and tube heat exchangers consist of a bundle, or bundles, of tubes installed axially inside a shell. The tubes end in tubesheets at each end of the shell, that separate the shell side fluid outside of the tubes from the tube side fluid inside the tubes. The tubes are supported by baffles that also create a flow pattern for the shell side fluid.

Figure 1-2 is a schematic drawing of a two-pass liquid/liquid heat exchanger. This is a very common design. Cooling water enters the water box from the bottom, flows through the bottom tube bundle and returns through the top bundle. The process fluid, in this case warm kerosene in a refinery, enters the shell from the top at the far end, follows the circulation pattern through the shell and exits at the bottom near the water box.

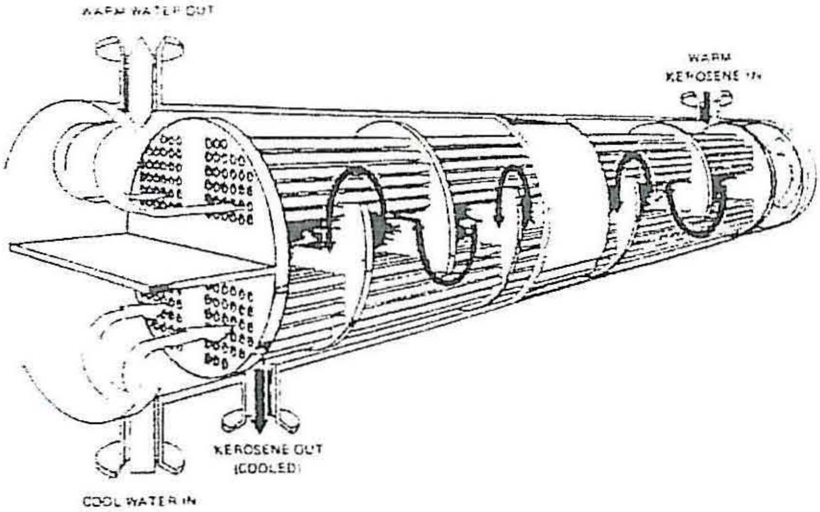


Figure 1-2. A liquid-liquid shell and tube heat exchanger.

Figure 1-3 shows a cutaway drawing of a steam surface condenser. Cooling water flow in this unit is the same as in Figure 1-1. Steam enters the top of the shell at the center, condenses as it flows over the tube surfaces, and exits to a hot well or condensate receiver at the bottom of the shell, not shown in this drawing.

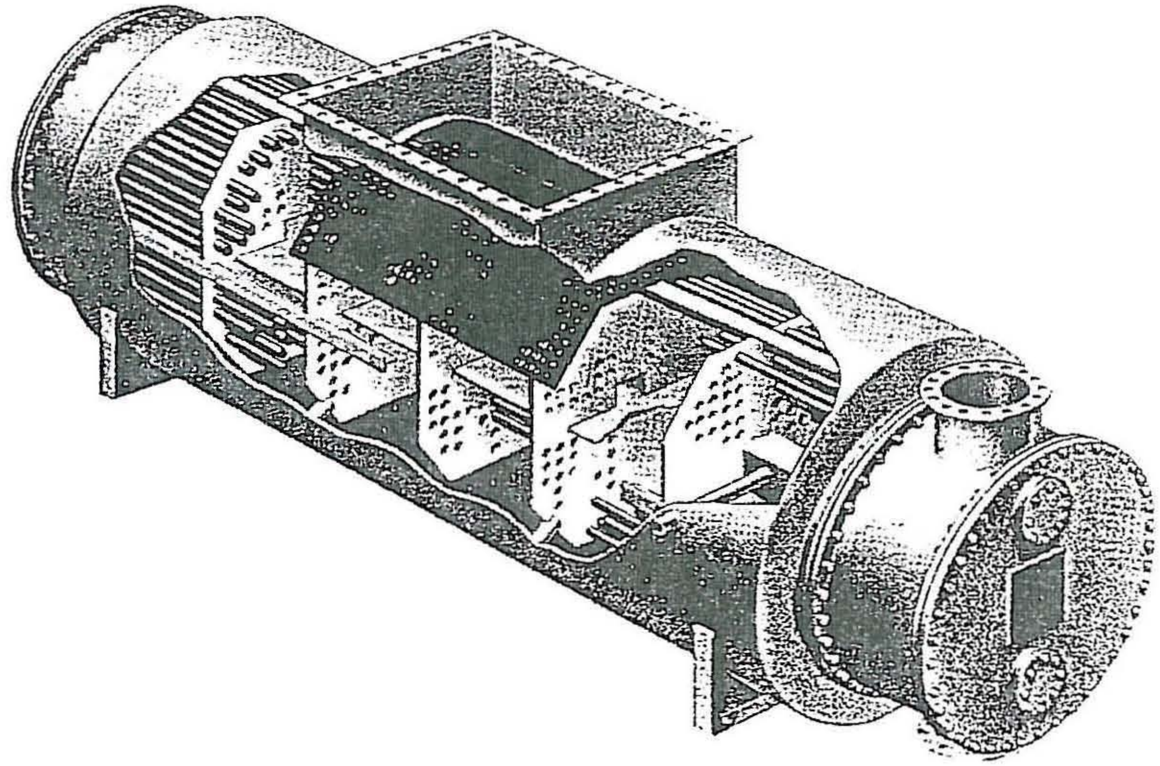


Figure 1-3. Cutaway view of a steam surface condenser.

The units shown in Figures 1-2 and 1-3 are typical of many different but similar shell and tube heat exchanger designs. Water may be on either the shell side or the water side, depending on process requirements. Sizes range from small lubricating oil coolers, containing just a few tubes, to very large power station surface condensers containing many thousands of tubes. Cooling water operations involving shell and tube heat exchangers are discussed in chapter 4.

2.3.2 Skin Temperatures

In a shell-and-tube heat exchanger, skin temperatures are defined as the tube wall temperatures that would be measured by thermocouples embedded at the water and process side metal surfaces. Skin temperatures are functions of heat transfer coefficients and flow rates in the system, and they are strongly affected by deposits that build up on the tube walls. Skin temperatures can be measured in pilot scale units, but must be estimated in plant equipment, from fluid entering and exiting temperatures, heat transfer rates and fouling factors.

Consider water on the tube side of an operating shell and tube heat exchanger. The skin temperature inside the tubes will, in general, be from 10 to as much as 50 °F higher than the exiting water temperature, depending on heat flux and flow conditions. Without effective water treatment, deposits will tend to form on the inside tube walls. Deposits insulate the tube metal from the flowing water, and increase the resistivity of the water side film, reducing effective heat transfer. The tube side skin temperature increases, and this tends to further increase deposition. The result can be restricted water flow, lost cooling capacity and severe corrosion damage to tubes.

Clearly, as stated at the beginning of this chapter, the major objectives of water treatment must be to keep heat transfer surfaces clean and free from corrosion damage. Water treatment in cooling water systems is discussed in chapter 4, and heat transfer technology in boiler systems is covered in chapter 3.

2.3.3 Other Heat Exchanger Designs

Shell and tube heat exchangers are the most widely used designs. They are simple to design, build and service; they have high throughput capacity; and they are relatively inexpensive. Other designs, however, are frequently found in special applications where space is limited and high heat transfer efficiency is required.

Plate and frame heat exchangers consist of an assembly of metal plates bolted together, with a series of gaskets that allows water to flow between the plates. Two different fluids flow between alternate plates, without mixing, and the plates become the heat exchange surfaces. Plate and frame designs pack high efficiency cooling into a relatively small space. They are used frequently in commercial buildings where space is limited, to separate primary and secondary cooling systems, and in open and closed cooling systems in free cooling designs. See chapter 4 for an explanation of these systems.

Spiral heat exchangers are used primarily in chemical manufacturing plants that require high efficiency cooling of small process streams. They can accommodate large temperature differences and, in some cases, corrosive liquids. Spiral units are often used to exchange heat between two specialty process fluids.

3.0 The Structure of Matter

This section covers basic information that is needed for understanding water chemistry and water treatment. Any first year college level inorganic chemistry textbook can be used to expand these topics and provide more basic chemistry background.

3.1 ELEMENTS AND THE PERIODIC TABLE

All matter is composed of various combinations of 98 different materials called elements. Each element has a name and a chemical symbol. Table 1-3 contains a list of some typical elements commonly encountered in water treatment work, and their symbols.

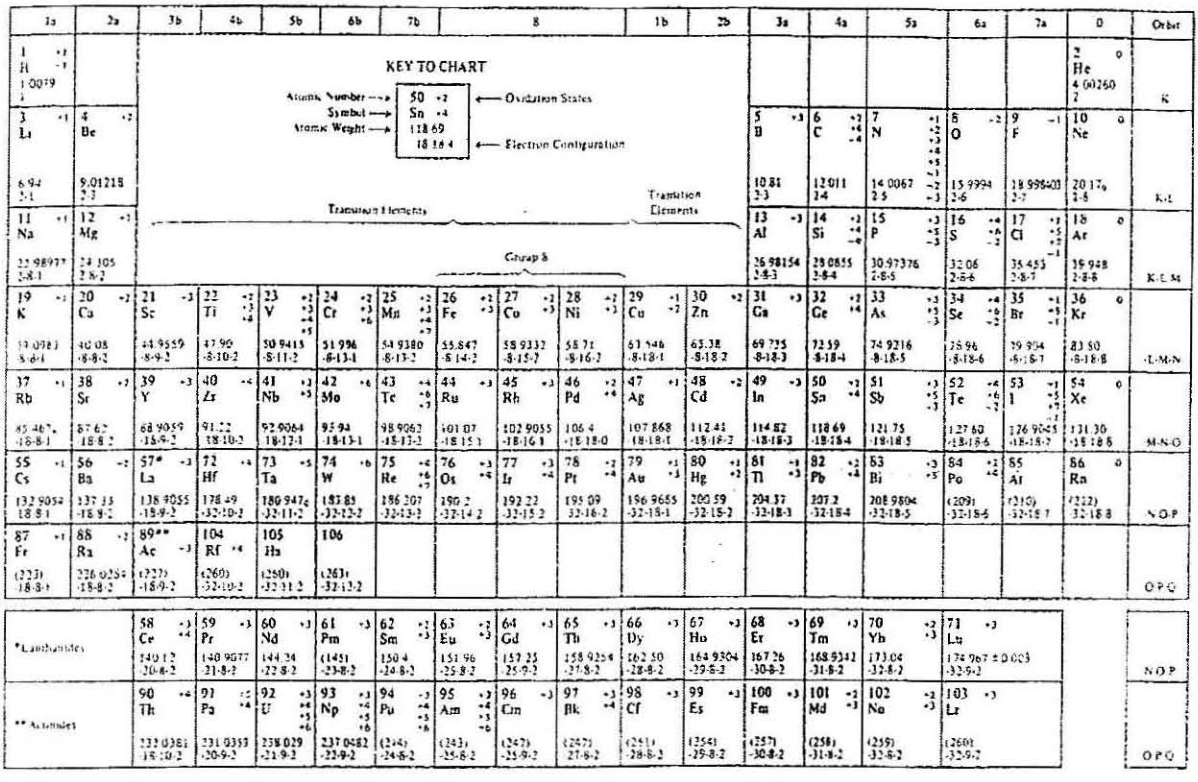
Table 1-3
Common Chemical Elements

Element	Symbol	Atomic No.	Atomic Wt.	Valence	Equiv. Wt.
Hydrogen	H	1	1.0	+1	1.0
Oxygen	O	8	16.0	-2	8.0
Sodium	Na	11	23.0	+1	23.0
Silicon	Si	14	28.1	+4	7.0
Phosphorus	P	15	31.0	+5	6.2
Sulfur	S	16	32.1	-2/+6	16.1/5.0
Chlorine	Cl	17	35.5	+1/-1	35.5
Calcium	Ca	20	40.1	+2	20.1
Iron	Fe	26	55.8	+2/+3	27.9/18.6

An atom is defined as the smallest unit of any element that retains all the chemical and physical properties of the element. Atoms consist of a nucleus containing positively charged protons, and neutrons that carry no charge. The nucleus provides most of the mass (weight) of the element. Surrounding the nucleus is an orbiting group of negatively charged electrons that balance the positive charge of the nucleus.

The properties of the elements fall into recurring patterns. This allows the elements to be arranged in a Periodic Table of the Elements, as shown in Figure 1-4. The elements are arranged in rows and numbered consecutively. These are the atomic numbers in Table 1-3. The periodic table is arranged in order of increasing atomic number. Elements in the same column have similar chemical properties. The atomic weight of each element represents the total number of protons and neutrons in the nucleus of the atom. The atomic weight of an atom will generally be close to twice its atomic number in the periodic table, as shown in Figure 1-4.

PERIODIC TABLE OF THE ELEMENTS



Numbers in parentheses are mass numbers of most stable isotope of that element

Figure 1-4. The periodic table of the elements.

The elements on the left side of the periodic table are called the metallic elements, and the elements on the right side, often gases at room temperature, are called the nonmetallic elements. These are loose definitions, however, because many elements, particularly those near the middle of the periodic table, can exhibit both metallic and nonmetallic properties.

3.2 CHEMICAL COMPOUNDS

The elements combine with each other in various ways, and also with themselves, to form molecules. Molecules that contain more than one element are called chemical compounds. A molecule is defined as the smallest unit of any substance that retains all the physical and chemical properties of that substance. For example:

- Two atoms of oxygen combine to form molecular oxygen, O_2.
- One atom of sodium and one atom of chlorine combine to form sodium chloride, or table salt, NaCl.

The molecular weight of a compound is the sum of the atomic weights of the elements in that compound. Hence, from the data in Table 1-3, the molecular weight of oxygen is 32, and the molecular weight of sodium chloride is 58.5.

Organic compounds, named from the compounds that make up living matter, consist primarily of compounds of carbon, hydrogen, nitrogen and oxygen, with small amounts of other elements. Inorganic compounds, including some simple compounds of carbon and oxygen, make up the nonliving matter - solids, liquids and gases – in the universe. This discussion of basic chemistry is concerned primarily with inorganic compounds.

3.3 IONIZATION AND VALENCE

When inorganic compounds dissolve in water, they ionize – that is, they separate into two or more electrically charged particles. For example, elements in column 1 of the periodic table (Figure 1-4) lose one electron and become ions with a charge of +1. Thus, when sodium chloride dissolves, the sodium atom loses one electron and becomes a sodium ion. The symbol for the sodium ion is Na^+. Similarly, the chlorine atom, in column 7 of the periodic table, accepts the electron from the sodium atom and becomes a negative chloride ion. Cl^-. The charge on an ion is called the valence. The sodium ion has a valence of +1 and the chloride ion has a valence of –1, as shown in Table 1-3.

Ions with a positive charge are called cations, and ions with a negative charge are called anions. These are electrochemical terms. Electrochemistry and corrosion are discussed in section 8 of this chapter.

It is a fundamental law of nature that in any stable system, electrical neutrality must always be preserved. This means that in any compound, or any solution of ionized dissolved solids, the total number of positive charges will always exactly equal the number of negative charges. This principle governs how compounds are formed and how they react in solution.

Elements in the second column of the periodic table lose two electrons when they ionize. Thus, the calcium ion, Ca^{+2}, has a valence of +2. According to the principle of electrical neutrality, when calcium reacts with chlorine to form calcium chloride, one calcium ion must combine with two chloride ions, and the formula for calcium chloride is $CaCl_2$.

3.3.1 Multivalent Elements

Some elements, because of the particular structure of the electron orbits around the nucleus, are able to ionize in more than one way. For example, iron can lose two electrons to form ferrous ions, Fe^{+2}, or it can lose three electrons to form ferric ions, Fe^{+3}. Some typical iron compounds are:

• Ferrous chloride – $FeCl_2$	Ferric chloride – $FeCl_3$
• Ferrous oxide – FeO	Ferric oxide (rust) – Fe_2O_3
• Ferrous hydroxide – $Fe(OH)_2$	Ferric hydroxide – $Fe(OH)_3$

Table 1-4 lists some of the other elements common in water solutions that can exist in different valence states:

Table 1-4
Valence States of Common Elements

Element	Valence	Typical Compounds
Chlorine	-1	Hydrochloric acid (muriatic acid) – HCl
	+1	Sodium hypochlorite (bleach) – $NaOCl$
	+4	Chlorine dioxide – ClO_2
Copper	+1	Cuprous oxide – Cu_2O; cuprous chloride – $CuCl$
	+2	Cupric oxide – CuO; cupric hydroxide – $Cu(OH)_2$
Manganese	+2	Manganous oxide – MnO
	+4	Manganese dioxide – MnO_2
	+7	Potassium permanganate –$KMnO_4$
Sulfur	-2	Hydrogen sulfide – H_2S
	+4	Sodium sulfite – Na_2SO_3
	+6	Sulfuric acid – H_2SO_4

The valence state of an element is sometimes referred to as its oxidation state. The higher the valence, the higher its oxidation state. This term derives from the fact that most naturally occurring minerals have been formed by reaction of metals with oxygen in the air. The elements in Table 1-4 can exist in other oxidation states besides those shown, and many other elements also have several oxidation states. Only the most common forms are shown in Table 1-4.

3.3.2 Complex Ions

Several elements form very stable ions containing groups of two or sometimes three elements. These groups, called complex ions, stay together and behave as a single ion in most chemical reactions. Following are some common complex ions that are very important in water chemistry:

- Ammonium – NH_4^+ Hypochlorite – OCl^- Sulfite – SO_3^{-2}
- Phosphate – PO_4^{-3} Hydroxide – OH^- Sulfate – SO_4^{-2}

Many other complex ions in addition to these are found in water solutions.

Oxygen always has a valence of –2, and hydrogen is always +1. It is therefore easy to calculate the valences of the other elements in complex ions containing hydrogen and oxygen. For example, the sulfur in the sulfate ion must have a valence (oxidation state) of +6, combined with four oxygen atoms, to give the complex ion a valence of -2.

As discussed earlier, electrical neutrality must be observed in compounds. Thus, the formula for trisodium phosphate is Na_3PO_4, and calcium hypochlorite is $Ca(OCl)_2$. Ammonium sulfate is a compound formed from two complex ions, $(NH_4)_2SO_4$.

3.4 CALCULATIONS

3.4.1 Equivalent Weights

Sodium chloride molecules contain one atom of sodium and one atom of chlorine. From Table 1-3, the atomic weight of sodium is 23 and the atomic weight of chlorine is 35. Atomic weights are relative numbers that can be expressed in any units. This means that 23 grams, or pounds of sodium will react with 35 grams, or pounds of chlorine to form 58 grams, or pounds of sodium chloride.

However, the situation is not always that simple. According to the formula for calcium chloride, one atom of calcium, or 40 grams, will combine with two atoms of chlorine, or 35 x 2 = 70 grams. The amount of calcium that will combine with one atomic weight, (35 grams) of chlorine is half of the atomic weight, or 20 grams.

The equivalent weight of an element is defined as the atomic weight divided by the valence. Thus, as shown in Table 1-3, the equivalent weight of sodium is 23 and the equivalent weight of calcium is 20. From the equivalent weights, it is possible to calculate the amounts of reactants needed for any chemical reaction, and the amounts of products that will form.

For example, calculate the amount of chlorine needed to react with 100 pounds of calcium to form calcium chloride:

$$Ca^{+2} + 2Cl^{-1} = CaCl_2 \tag{1-8}$$

Equivalent weights: Ca = 20, Cl = 35
Answer: 100 lb of Ca will combine with (100/20) x 35 = 175 lb of Cl

If an element can exist in several different valence states, it is important to choose the correct equivalent weight for each reaction. For example, in the compound ferrous chloride ($FeCl_2$), iron has a valence of +2, and the equivalent weight is 55.8/2 = 27.9. In ferric chloride ($FeCl_3$), iron has a valence of +3 and the equivalent weight is 55.8/3 = 18.6.

3.4.2 Molarity

Since chemical reactions are often carried out in water solutions, molecular weights and equivalent weights are used to determine quantities of solutions needed for reactions. The following definitions are used:

- Mole. A mole is 1 molecular weight of any substance expressed in grams. Thus, 1 mole of sodium is 23 grams and 1 mole of chlorine is 35.5 grams.
- Molar solution (M). A 1 M solution contains 1 molecular weight in grams of any substance in 1 liter of water, so that a 1 M solution of sodium chloride contains 58.5 grams of NaCl per liter. Similarly, a 1-millimolar solution contains 1 molecular weight in milligrams of any substance per liter.

- ppm and mg/L. A 1 millimolar solution of NaCl contains 58.5 milligrams per liter (mg/L), or 58.5 parts per million (ppm). Mg/L measures weight/volume, while ppm measures weight/weight. In the dilute solutions normally used in water treatment work, mg/L is the same as ppm. However, in concentrated brines and seawater, and in some ion exchange applications, ppm becomes a smaller number than mg/L, because the density of the solution is appreciably greater than 1. The conversion factor is: ppm x density = mg/L. In this manual, mg/L is used throughout to avoid any confusion.

As explained in section 3.4.1, equivalent weights are used to determine how elements in different valence states will combine. The same concept applies to solutions:

- Equivalent. An equivalent of any substance is its equivalent weight expressed in grams. Thus, 1 equivalent of calcium is 20 grams.
- Normality (N). A 1 N solution contains 1 equivalent weight of any substance in grams, in 1 liter of water. A 1N solution of ferric chloride, $FeCl_3$, contains (55.8 + 35.5x3)/3 = 54.1g/L (see section 3.4.1).

Equivalent weights and normality are very important in analytical work. For example, if 10 ml. of 0.02N sulfuric acid are needed to titrate 100 ml. of a solution of sodium hydroxide, what is the concentration of the sodium hydroxide solution? From the definition of normality, above, a 0.02N solution contains 0.02 equivalent/liter, or 20 milliequivalents/liter. Thus, 10 ml of this solution contains 0.2 milliequivalent of sulfuric acid. Since the equivalent weight of sodium hydroxide is 40, 40 x 0.2 = 8 mg of caustic in 100 ml of solution, or 80 mg/L (80 mg/L). The equation for determining the milligrams (mg) of a substance in a sample is:

$$\text{(ml titrant)} \times \text{(normality of titrant)} \times \text{(equiv. wt.)} = \text{mg.} \qquad (1\text{-}9)$$

These definitions are very important and will be used throughout this manual in discussing water analyses and concentrations of chemicals used in water treatment. Normality and titration calculations are discussed further in section 6.2 in this chapter.

3.4.3 Use of Common Denominators for Calculations ($CaCO_3$ equivalents)

For calculation purposes, elements and compounds are like apples and oranges. The amounts of each element or compound in a reaction must be converted to a common denominator before they can be added and subtracted. One easy way to do this is to convert the amount of each substance into equivalents by dividing by its equivalent weight. This method is often used to check the accuracy of analytical work (see section 10.2.1 in this chapter).

Instead of using equivalents directly, it is a simple matter to convert an amount of any substance to an equivalent amount of any other substance, by simply calculating the ratio of equivalent weights. For example, convert 100 mg/L of calcium in solution to an equivalent amount of calcium carbonate:

Equivalent weight of Ca^{+2} = 20
Equivalent weight of $CaCO_3$ = 50
100 mg/L Ca x 50/20 = 250 mg/L $CaCO_3$

Thus, the conversion factor for calcium to calcium carbonate is 2.5. Calcium carbonate equivalents is the most common method used to report hardness and alkalinity in water, and to do water softening calculations. Alkalinity and hardness are explained in sections 6.4 and 7.2.2 in this chapter, and softening is covered in chapter 2.

4.0 Chemical Equilibrium

4.1 SALTS

Salts are compounds of a positively charged metallic ion with a negatively charged nonmetallic ion. Salts are generally formed by reaction of an acid and a base in solution (see section 4.2, below). Some typical salts that are important in water chemistry include:

Sodium chloride	– $NaCl$	Calcium carbonate	– $CaCO_3$
Calcium sulfate	– $CaSO_4$	Sodium bromide	– $NaBr$
Trisodium phosphate	– Na_3PO_4	Magnesium silicate	– $MgSiO_3$

Most inorganic salts are completely ionized in solution. That is, no molecules of sodium chloride, calcium carbonate, etc. exist in solution. They are all dissociated into sodium, calcium, bromide and carbonate ions. Writing this as a chemical equation for trisodium phosphate:

$$Na_3PO_4 \rightarrow 3Na^+ + PO_4^{-3} \qquad (1\text{-}10)$$

Be careful not to confuse ionization with solubility. Some salts, for example sodium bromide, are very soluble; others, for example calcium carbonate, are only slightly soluble. In either case, whatever is dissolved is completely ionized. Solubility of salts is discussed in section 5 in this chapter. Reactions of metal ions with water (hydrolysis reactions) are discussed in section 4.3.5.

4.2 ACIDS AND BASES

There are many definitions of acids and bases. For purposes of water chemistry, an acid is a compound that ionizes in water to produce hydrogen ions, or that will neutralize a base. A base is a compound that produces hydroxide ions in water, or that will neutralize an acid.

Some inorganic acids and bases, like salts, are completely ionized in water. These are called "strong" acids and bases. Two very common examples are hydrochloric (muriatic) acid and sodium hydroxide (caustic):

Hydrochloric acid $HCl \rightarrow H^+ + Cl^-$
Sodium hydroxide $NaOH \rightarrow Na^+ + OH^-$

Hydrochloric and sulfuric acids are also known as mineral acids. Strong acids and bases react with, or neutralize each other completely. The product of the reaction of a strong acid and a strong base in water is an ionized salt and water. For example, hydrochloric acid and sodium hydroxide react to form sodium chloride and water.

$$H^+ + Cl^- + Na^+ + OH^- \rightarrow Na^+ + Cl^- + HOH\ (H_2O) \qquad (1\text{-}11)$$

However, not all acids and bases behave this way. Sometimes the acid or base does not ionize completely, or it ionizes in stages. These are called "weak" acids and bases. A typical example is hypochlorous acid (HOCl). The sodium salt of hypochlorous acid is sodium hypochlorite (bleach solution). Hypochlorous acid ionizes to form hypochlorite ions and hydrogen ions:

$$HOCl \leftrightarrow OCl^- + H^+ \qquad (1\text{-}12)$$

However, the ionization is not complete. Note that the arrow in equation (1-12) points in both directions. This means that whenever HOCl is added to water, some of the unionized acid remains. The ratio of the ionized products, OCl^- and H^+, to the unionized hypochlorous acid in solution is always a constant, as shown in equation (1-13):

$$\frac{[OCl^-][H^+]}{[HOCl]} = K_a = 3.0 \times 10^{-5} \qquad (1\text{-}13)$$

K_a is the ionization constant, or dissociation constant, for hypochlorous acid. An equilibrium exists between the ionized and unionized forms of the acid. If more hydrogen ions (acid) or more hypochlorite ions are added to the solution, the equilibrium in equation (1-12) will shift to the left, to maintain the same value of K_a. Thus, there is never a situation in which reaction (1-12) goes all the way to the right, so that all the hydrogen ions are available.

Many weak acids are dibasic or tribasic. This means that the acid molecule contains two or three hydrogen atoms, so that the acid can neutralize two or three moles of a monovalent base such as sodium hydroxide. A dibasic acid will ionize in two steps, as shown in equations (1-14) and (1-15) for carbonic acid, and it will have two ionization constants. These are numbered K_1 and K_2.

$$H_2CO_3 \leftrightarrow HCO_3^- + H^+ \qquad (1\text{-}14)$$
$$HCO_3^- \leftrightarrow CO_3^{-2} + H+ \qquad (1\text{-}15)$$

Table 1-5 shows ionization constants for some weak acids and bases that are important in water treatment.

Table 1-5
Dissociation Constants for Weak Acids and Bases at 25 °C

Acid	Dissociation	Ionization Constant
Boric acid	$H_3BO_3 \leftrightarrow H^+ + H_2BO_3^-$	$K_1 = 7.3 \times 10^{-10}$
	$H_2BO_3^- \leftrightarrow H^+ + HBO_3^{-2}$	$K_2 = 1.8 \times 10^{-13}$
	$HBO_3^{-2} \leftrightarrow H^+ + BO_3^{-3}$	$K_3 = 1.6 \times 10^{-14}$
Carbonic acid	$H_2CO_3 \leftrightarrow H^+ + HCO_3^-$	$K_1 = 4.3 \times 10^{-7}$
	$HCO3^- \leftrightarrow H^+ + CO_3^{-2}$	$K_2 = 5.6 \times 10^{-11}$
Hypobromous acid	$HOBr \leftrightarrow H^+ + OBr^-$	$K_1 = 2.1 \times 10^{-9}$
Hypochlorous acid	$HOCl \leftrightarrow H^+ + OCl^-$	$K_1 = 3.0 \times 10^{-5}$
Phosphoric acid	$H_3PO_4 \leftrightarrow H^+ + H_2PO_4^-$	$K_1 = 7.5 \times 10^{-3}$
	$H_2PO_4^- \leftrightarrow H^+ + HPO_4^{-2}$	$K_2 = 6.2 \times 10^{-8}$
	$HPO_4^{-2} \leftrightarrow H^+ + PO_4^{-3}$	$K_3 = 2.2 \times 10^{-13}$
Ammonium hydroxide	$NH_4OH \leftrightarrow NH_4^+ + OH^-$	$K_1 = 4.8 \times 10^{-5}$

The more negative the ionization constant – that is, the larger the negative exponent of 10, the weaker the acid and the less the tendency to ionize and form hydrogen ions in solution. Thus, the second and third ionization constants, K_2 and K_3, of a weak acid or base, will always be smaller than K_1.

The concept of weak acids and bases is very important in water preparation and in boiler and cooling water treatment, and will be discussed further in chapters 2, 3 and 4.

4.3 THE IONIZATION OF WATER

Water is a special case. From the formula, H_2O or HOH, it is clear that water is both an acid and a base. That is, it can, and does, ionize to form both hydrogen and hydroxide ions in solution:

$$\mathrm{HOH} \leftrightarrow \mathrm{H^+} + \mathrm{OH^-} \qquad (1\text{-}16)$$

Water is a very weak acid and base. The ionization constant for water is 10^{-14} at room temperature. Since the concentration of unionized water in any solution is, obviously, very large compared to other constituents, it is considered as a constant and ignored. Therefore, the ionization equilibrium equation for water is written simply as the ion product:

$$[\mathrm{H^+}][\mathrm{OH^-}] = K_{w\,(25°C)} = 1.0 \times 10^{-14} \qquad (1\text{-}17)$$

4.3.1 Definition of pH

In a sample of pure demineralized and degasified water, it is obvious from reaction (1-16) that the concentrations of hydrogen and hydroxide ions must be equal. Concentrations in equilibrium equations such as (1-17) are expressed in moles per liter. Also, it is a rule of mathematics that exponents add in multiplication. Thus, it follows that in pure water at room temperature, $[\mathrm{H^+}] = [\mathrm{OH^-}] = 10^{-7}$. Equation (1-17) then becomes:

$$K_{w\,(25°C)} = [\mathrm{H^+}][\mathrm{OH^-}] = [10^{-7}][10^{-7}] = 10^{-14} \qquad (1\text{-}18)$$

Because of the great importance of acid and base concentrations in water chemistry, chemists devised a simple way to refer to these concentrations. They defined a function, pH, as the negative logarithm of the hydrogen ion concentration. Thus:

$$\mathrm{pH} = -\log_{10}[\mathrm{H^+}] \qquad (1\text{-}19)$$

In pure water, at room temperature, therefore:

$$\mathrm{pH} = -\log_{10}[10^{-7}] = 7 \qquad (1\text{-}20)$$

Equation (1-19) is the fundamental equation defining pH. Equation (1-20) shows why pure water is said to have a pH of 7. Since the hydroxide ion concentration, $[\mathrm{OH^-}]$, is also 10^{-7} from equation (1-18), the pOH = 7. Thus, pure water at pH 7 is said to be "neutral"; that is, it is neither acidic nor basic.

The pH concept is fundamental to an understanding of water chemistry and to control of pretreatment systems, boilers and cooling towers. All of these systems depend on either precise pH control or on maintaining the pH above a specified minimum level. Unexpected changes in pH are usually a warning of problems that must be corrected quickly.

4.3.2 pH Calculations

The pH of any water solution measures the concentration of hydrogen ions, or the acid strength of the solution. For example:

- What is the pH of a 0.01M solution of hydrochloric acid?

$$pH = -\log[H^+] = -\log[10^{-2}] = 2$$

- If the pH of a solution is 9, what is the hydroxide ion concentration?

$$K_w = [H^+][OH^-] = [10^{-9}][OH^-] = 10^{-14}$$
$$[OH^-] = 10^{-14}/10^{-9} = 10^{-5}\text{ molar}$$

It is important to remember that pH is a logarithmic function. Figure 1-5 is a graph of pH versus hydrogen and hydroxide ion concentrations. This graph shows clearly that as required by equation (1-18), the product of the hydrogen and hydroxide ion concentrations must always be 10^{-14}.

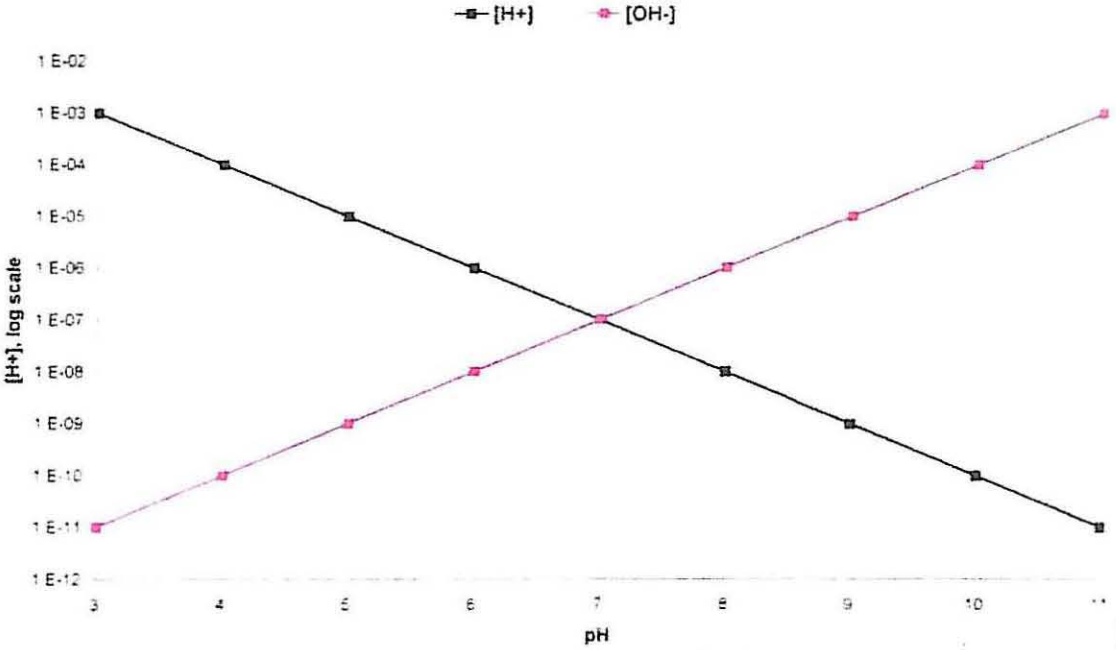


Figure 1-5. pH vs. hydrogen and hydroxide ion concentrations.

For example, from Figure 1-5 at pH = 8:

$$[H^+] = 10^{-8}\text{ molar}$$
$$[OH^-] = 10^{-6}\text{ molar}$$
$$[H^+] \times [OH^-] = [10^{-8}] \times [10^{-6}] = 10^{-14}$$

Clearly, at the ambient temperature neutral point, the hydrogen and hydroxide in concentrations are equal, at 10^{-7} molar.

Each unit change in pH represents a one log unit change, or a factor of 10, in $[H^+]$ and $[OH^-]$. Thus, if 1 mg/L of acid is needed to change the pH of a solution from 8 to 7, then 10 mg/L will be needed to reach pH = 6, 100 mg/L to reach pH = 5 and 1000 mg/L to reach pH = 4. This explains why a relatively small amount of acid or base can make a large change in pH around the neutral range from pH 6 to 8, but much larger amounts of acid or base are required to move the pH below 5 or above 9. These relationships can be seen clearly in Figure 1-6. Note that in Figure 1-6, the "Y" axis is a logarithmic scale.

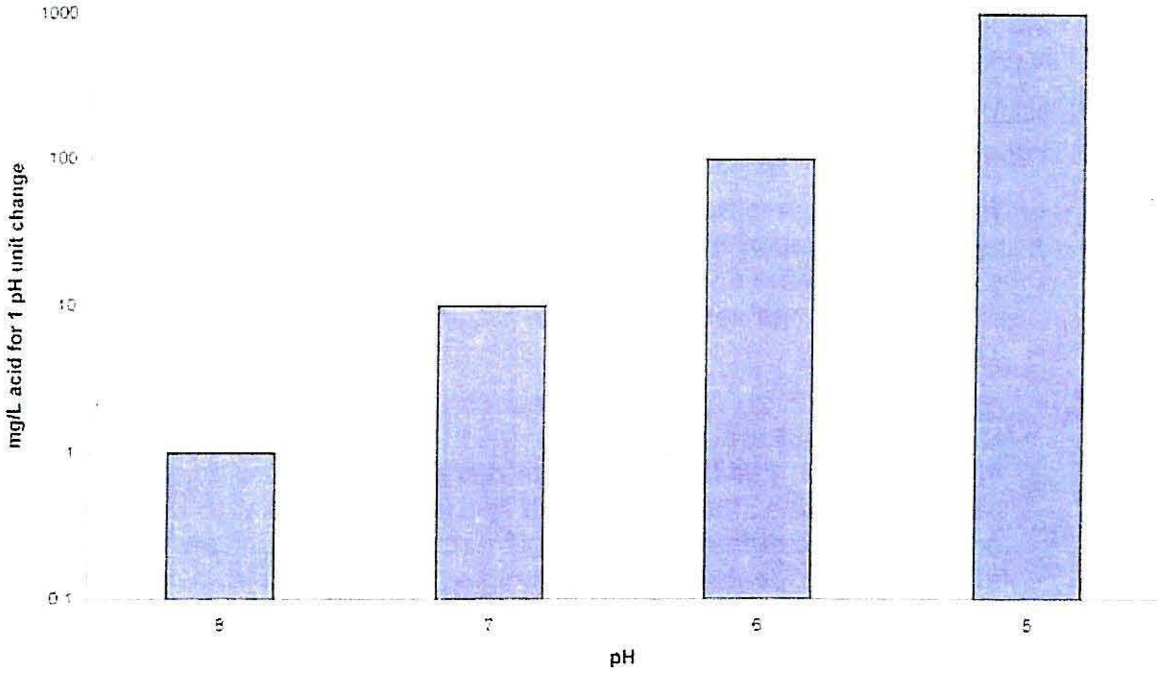


Figure 1-6. Acid requirements vs. pH.

4.3.3 Effect of Temperature on pH

The dissociation, or ionization of weak acids and bases increases with temperature. That is, the equilibrium in equations (1-12), (1-14) and (1-15) shifts towards the right side of the equation, and the ionization constants in Table 1-5 all move to higher values.

Table 1-6 shows how increasing temperature changes K_w, the ionization constant for water.

TABLE 1-6
Effect of Temperature on the Ionization of Water

Temp. °C/°F	Pressure, psig	Kw
25/77	14.7	10^{-14}
100/212	14.7	10^{-12}
200/392	200	10^{-11}

From equation (1-18), if K_w changes from 10^{-14} to 10^{-12} in boiling water, the pH must change from 7 to 6. Thus, the pH of pure water at the boiling point is 6, not 7, even though the water is still neutral (meaning equal molar concentrations of hydrogen and hydroxide ions). Since practical pH measurements are made at many different temperatures, the temperature of the water must be considered when comparing data. To correct for this error, most pH meters automatically compensate for temperature and report pH data calculated at 25 °C. However, pH measurements using color wheels or pH papers are not automatically compensated. Therefore, when these methods are used, the water sample should be cooled to room temperature before the measurement is taken.

4.3.4 pH Measurements

There are three general methods for measuring the pH of water samples:

- Titration, with a standard solution of a strong base, normally sodium hydroxide. Titration is used when very accurate data are required, when components of the solution interfere with electrode or color measurements, or at very low and very high pH values where electrodes and color wheels lose sensitivity.
- pH meters, using a membrane electrode, usually glass. Laboratory grade pH meters can be sensitive to 0.01 pH unit or smaller, for critical measurements. Field grade meters range from reliable hand-held meters with separate electrodes, to simple "pen-type" meters with both the meter and the electrodes in a single small unit. Successful field pH measurements depend upon: a) keeping the electrodes clean and moist; and b) frequent calibration with reliable standard solutions. Pen-type meters should be calibrated before each use and should be discarded when they produce unstable readings or cannot be calibrated. With care, measurements to ± 0.1 pH unit are practical. pH meters are not reliable below pH 3 or above pH 11. Some solutions containing high turbidity or high levels of oxidizing agents may interfere with electrode pH measurements.
- Colorimetric methods, using color comparator solutions or papers impregnated with pH-sensitive dyes. Colorimetric methods are fast and inexpensive, and for many applications such as routine cooling water testing, are sufficiently accurate. Measurements are usually no better than

± 0.5 pH unit. Color and turbidity in the test sample will interfere and may make colorimetric readings impossible.

4.4 REACTIONS OF SALTS WITH WATER (HYDROLYSIS)

Salts of strong bases and strong acids, such as sodium chloride ($NaCl$) and potassium nitrate (KNO_3), are neutral. These salts do not react with water and do not change the pH of the solution.

Salts of weak acids with strong bases, and weak bases with strong acids, behave differently. Because weak acids and bases are not completely ionized, they react with hydrogen and hydroxide ions from the ionization of water (equation 1-14), to produce unionized acid or base as required by the appropriate dissociation constant (Table 1-5).

To illustrate this process, consider ferric chloride ($FeCl_3$), a very common salt in cooling water systems. Ferric chloride is a salt of a weak base, ferric hydroxide, and a strong acid, hydrochloric acid. Ferric chloride is completely ionized:

$$FeCl_3 \rightarrow Fe^{+3} + 3Cl^- \qquad (1\text{-}21)$$

Because ferric hydroxide is a weak base, ferric ions will react with the hydroxide ions from the ionization of water to form unionized ferric hydroxide. This is a reversible, equilibrium reaction. It is simply the reverse of the dissociation reaction of ferric hydroxide (Table 1-5):

$$Fe^{+3} + 3HOH \leftrightarrow Fe(OH)_3 + 3H^+ \qquad (1\text{-}22)$$

Equations (1-21) and (1-22) can be added together to show the overall reaction that occurs when ferric chloride dissolves in water:

$$FeCl_3 + 3HOH \rightarrow Fe(OH)_3 + 3H^+ + 3Cl^- \qquad (1\text{-}23)$$

Reactions of salts with water that change the pH of the solution are called hydrolysis reactions. Comparing equations (1-21) and (1-23), the overall effect is to replace ferric ions in solution with hydrogen ions. This makes the solution acid and lowers the pH. Equation (1-23) is an important part of the corrosion reactions that occur on steel in water. Corrosion is discussed in section 8 of this chapter and in chapters 3 and 4.

5.0 Solubility

5.1 INTRODUCTION

Solubility refers to the tendency of a substance to dissolve in (mix with) a fluid such as water, without any change in chemical composition other than ionization. Table salt and sugar both dissolve easily in water. The salt ionizes; sugar, as an organic compound, does not. However, the salt and sugar can both be recovered unchanged simply by evaporating the water.

Water has often been called the "universal solvent" because of its ability to dissolve at least a small amount of almost any substance. Sometimes these amounts are very small and are ignored. However, it is important not to confuse solubility with other processes, such as corrosion. A piece of steel left in unprotected water will corrode. The water will turn yellow and analysis will show high levels of iron in the water. This is not solubility. It is the result of reaction of the iron with dissolved oxygen in the water. The iron in the water can be recovered only as various oxides of iron, not as iron metal, by evaporating the water. Corrosion is considered in Section 8.0 of this manual.

5.2 "RULES OF THUMB" FOR SOLUBILITY

Several general rules are available that aid in predicting the solubilities of various substances:

- Salts of sodium and potassium in group 1 of the periodic table, and ammonium (NH_4^+) salts, are generally soluble.
- The mineral acids (sulfuric, hydrochloric and nitric acids) are soluble.
- Halides (salts of chlorine, bromine and iodine in group 7 of the periodic table) are soluble, except for salts of silver, lead and a few other heavy metals. However, fluorides (also in group 7) are mostly insoluble.
- With the exception of the group 1 salts, carbonates, phosphates, sulfates and hydroxides tend to be slightly soluble. Nitrates are soluble.
- With the exception of the halides, salts of the group 2 and 3 elements plus iron, chromium and nickel, are slightly soluble.

5.3 SOLUBILITY PRODUCTS

Saturated solutions of slightly soluble salts will generally be in equilibrium with the solid salt. For example: The solubility of calcium carbonate at ambient temperature is roughly 30 mg/L. A cooling system containing calcium carbonate scale will also have 30 mg/L of calcium carbonate in solution. As long as there is solid calcium carbonate present, and as long as the temperature remains constant, there will never be any more or less than 30 mg/L of calcium carbonate in solution at equilibrium.

In a saturated solution of any salt, the concentration of the salt in solution will be a constant, changing only with temperature. Since salts are completely ionized (section 4.1), the product of the ions in solution can be written as a constant, called the solubility product. Again using calcium carbonate as an example:

$$K_{sp} = [Ca^{+2}][CO_3^{-2}] = 5 \times 10^{-9} \qquad (1\text{-}24)$$

This equation is similar to the ion product constant for water, as shown in equation (1-18).

Table 1-7 shows typical solubility products for some slightly soluble compounds common in water systems:

TABLE 1-7
Common Solubility Products at 25 °C

Compound	Formula	Ion Product	K_{sp}
Calcium carbonate	$CaCO_3$	$K_{sp} = [Ca^{+2}][CO_3^{-2}]$	5.0×10^{-9}
Calcium sulfate	$CaSO_4$	$K_{sp} = [Ca^{+2}][SO_4^{-2}]$	2.0×10^{-4}
Ferrous hydroxide	$Fe(OH)_2$	$K_{sp} = [Fe^{+2}][OH^-]^2$	1.0×10^{-14}
Ferric hydroxide	$Fe(OH)_3$	$K_{sp} = [Fe^{+3}][OH^-]^3$	2.0×10^{-39}
Magnesium hydroxide	$Mg(OH)_2$	$K_{sp} = [Mg^{+2}][OH^-]^2$	1.2×10^{-11}
Magnesium carbonate	$MgCO_3$	$K_{sp} = [Mg^{+2}][CO_3^{-2}]$	2.9×10^{-5}
Zinc hydroxide	$Zn(OH)_2$	$K_{sp} = [Zn^{+2}][OH^-]^2$	1.8×10^{-14}

Using the ion product equations and known values of one component, it is possible to calculate the concentration of the other component in any solubility product. For example, by adding calcium, as calcium oxide (lime), to a solution, it is possible to reduce the amount of alkalinity (carbonate) in the water, to maintain the calcium carbonate solubility product. Similarly, by adding carbonate, as soda ash, the amount of calcium hardness can be reduced. This is the basis of the cold lime softening process discussed in chapter 2.

5.4 EFFECT OF TEMPERATURE ON SOLUBILITY

Most compounds become more soluble as the temperature of the solution increases, so that the solubility products become larger (less negative) at higher temperatures.

However, for some compounds that are very important in water treatment, the opposite is true. The most well known example is calcium carbonate. Calcium carbonate shows inverse solubility – that is, the solubility decreases with increasing temperature, so that the solubility product becomes smaller. This explains why calcium carbonate scale forms preferentially on the hottest surfaces in the system, usually the heat exchanger or boiler tubes. Mineral scale formation is discussed in section 7 in this chapter, and in chapters 3 and 4 covering boiler water and cooling water treatment.

Other compounds, including some forms of calcium phosphate, also are inversely soluble. The solubility of gypsum (calcium sulfate dihydrate, $CaSO_4 \cdot 2H20$) increases slowly with temperature to about 100 °F and then decreases. When water and operating conditions allow any of these salts to form, the chemical treatment program must be adjusted, recognizing their decreased solubility under heat transfer conditions. This problem is discussed in more detail in chapter 4.

5.5 MEASURING DISSOLVED SOLIDS IN WATER

5.5.1 Total Dissolved Solids

The most accurate way to measure total dissolved solids (TDS) in water is to evaporate a known volume and dry it to constant weight. For this purpose, the sample should be dried at no more than 110 °C, to avoid decomposing volatile compounds or driving off water of hydration (that is, water bound in the crystal structure of many compounds as they precipitate from water).

TDS measurements by this method include both ionized salts and any nonvolatile organic matter in the solution. To avoid including suspended insoluble matter, it is important to filter the sample before evaporation.

5.5.2 Conductivity

TDS by evaporation is a time-consuming laboratory procedure. For most routine purposes, such as control of cooling tower cycles of concentration (chapter 4), an approximate TDS measurement is sufficient. The electrical conductivity of the water serves this purpose very well. Conductivity measures only the ionic solids in the water.

A conductivity probe consists of two electrodes connected to a power supply in the control unit. The controller applies a small potential (voltage) difference to the electrodes and measures the resulting current. This current is proportional to the conductivity of the water, which in turn is a measure of the number of ions in the water that can carry current. The controller reports this current in micromhos per centimeter, or simply micromhos (μmhos). A modern unit for this measurement is microsiemens per centimeter, or μS/cm.

The current generated in this way is a function of the number of mono, di and trivalent cations and anions in the solution. For dilute water solutions, the conductivity is linear with ionic salt concentration, but the actual conductivity values vary with the specific ions in the solution. Also, the conductivity increases with temperature because higher temperature increases the diffusion rate of ions in the solution.

For these reasons, conductivity is only an approximation of the correct ionic dissolved solids content. As a "rule of thumb", the dissolved solids value is usually between about 65 to 75 percent of the measured conductivity.

5.5.3 Salinity

In concentrated salt solutions, such as seawater and saline well water, salinity is often used to represent dissolved ionic solids. Salinity was originally calculated from measured conductivity data using complicated formulas. However, for practical work in brines and seawater, a simple formula based on the chloride content of the water is used:

$$S = 1.806 \times Cl^- \qquad (1\text{-}25)$$

In this formula, chloride is expressed in grams per liter (g/L). The conversion is simple: 1 g/L = 1000 mg/L. Because of the high density of these concentrated salt solutions, data should not be expressed in ppm unless the density of the solution is known (see section 3.4.2 in this chapter).

5.6 SOLUBILITIES OF GASES IN WATER

Dissolved gases in water play very important roles in water chemistry, and it is therefore important to understand how gases behave in solution. Three laws of chemistry govern this behavior:

- Dalton's Law states that in any mixture of gases, the total pressure is the sum of the partial pressures of the individual gases in the mixture. For example, air is roughly 20 percent oxygen and 78 percent nitrogen. If a vessel contains air at 100 mm. total pressure, the partial pressure of oxygen will be 20 mm and the partial pressure of nitrogen will be 78 mm.
- Henry's Law states that the solubility of any gas is proportional to its partial pressure in the gas phase above the solution. The solubility of oxygen in water exposed to air at room temperature is 8 mg/L. If the air pressure is doubled, the solubility will increase to 16 mg/L.
- Inverse Solubility: All gases, regardless of their solubility, are inversely soluble: that is, the solubility decreases with increasing temperature, as explained in section 5.3. One theory explaining this is that increasing the temperature increases the vapor pressure of the water itself. This adds another component to the gas phase, thus reducing the partial pressure of each component gas.

5.6.1 Ionizing and Nonionizing Gases

For water chemistry purposes, gases can be divided into two groups: ionizing and nonionizing gases, sometimes called reactive and nonreactive gases. Nonionizing gases do not react directly with water, although they may react vigorously with other substances in the water. The solubilities of nonionizing gases in water are relatively low, but nevertheless very important. Oxygen and nitrogen are typical nonionizing gases.

Ionizing gases, on the other hand, do react directly with water, and for that reason their solubilities are much higher. Carbon dioxide, sulfur dioxide, hydrogen sulfide and nitrogen oxides are typical ionizing gases encountered in water treatment.

5.6.2 Oxygen – A Typical Nonionizing Gas

Dissolved oxygen in water is a major factor affecting water system operations and water treatment programs. Oxygen supports aquatic and microbiological life. Oxygen causes corrosion, and at the same time assists in forming passive, protective films on metal surfaces. Some water treatment programs require dissolved oxygen for good performance, while others work best in the absence of oxygen (chapter 4).

Figure 1-7 shows the solubility of oxygen in water as a function of temperature and pressure. At 0 °C and atmospheric pressure, the solubility is about 13 mg/L. At 25 °C it is roughly 8 mg/L, and in boiling water the solubility is zero. Most natural water supplies contain dissolved oxygen. Rain and surface waters are usually saturated, while well waters may be low in oxygen due to chemical and microbiological reactions.

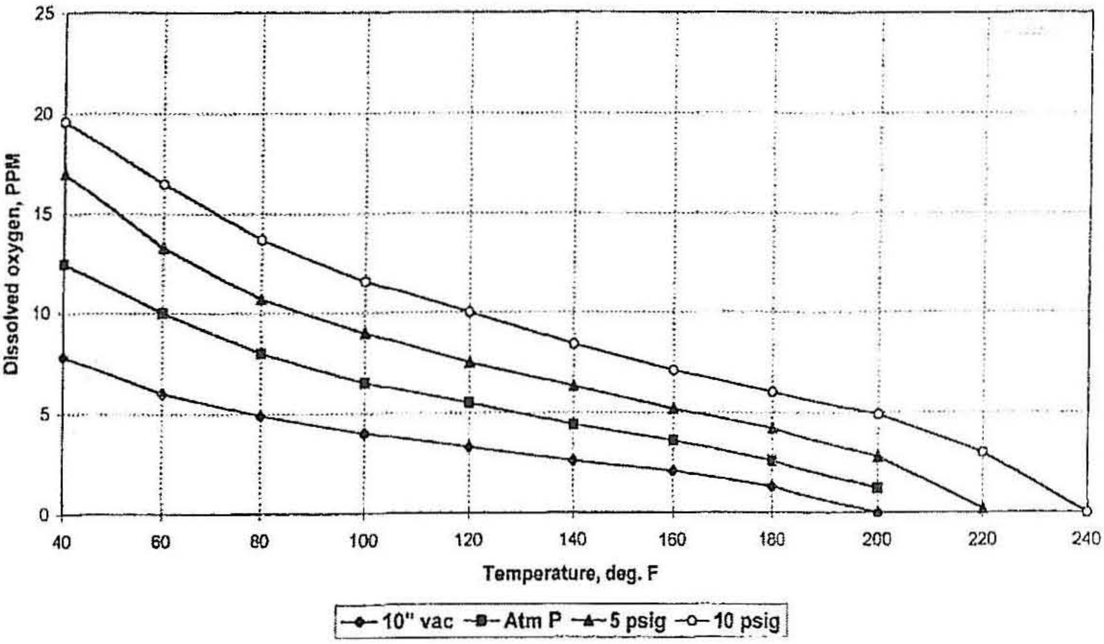


Figure 1-7. Solubility of oxygen in water vs. temperature.

Deaerators and oxygen scavengers are used to keep boiler water and condensate systems oxygen-free (chapter 3). Closed cooling systems also should be oxygen-free, but open cooling tower systems work best with water saturated with oxygen (chapter 4).

5.6.3 Carbon Dioxide – A Typical Ionizing Gas

Carbon dioxide dissolved in water is at least as important as dissolved oxygen in water treatment operations. Air contains only 0.03 percent carbon dioxide, compared to 20 percent oxygen, but because carbon dioxide reacts with water, its solubility is much greater than the solubility of oxygen. Figure 1-8 shows the solubility of carbon dioxide in water. At room temperature and atmospheric pressure, the solubility is about 1500 mg/L.

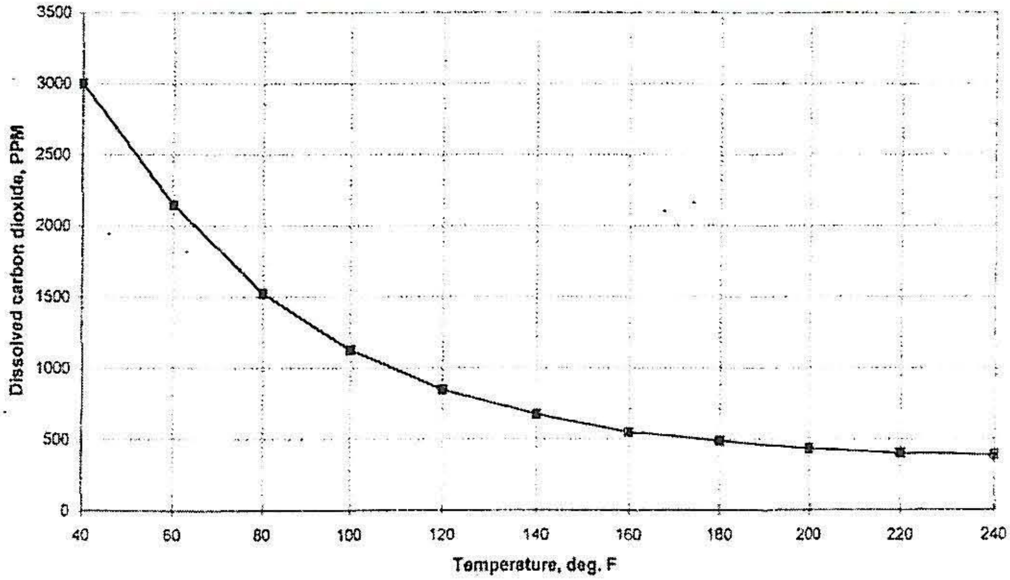


Figure 1-8. Solubility of carbon dioxide in water vs. temperature.

Carbon dioxide reacts with water to form carbonic acid. This reaction is one cause of corrosion in steam condensate lines (chapter 3). Carbonic acid is a very weak acid. It reacts further with water to produce bicarbonate and carbonate ions that are the source of carbonate scale on heat transfer surfaces. At the same time, bicarbonate ions provide helpful corrosion protection in alkaline cooling systems. Section 6 in this chapter is devoted to the chemical reactions of carbon dioxide in water.

5.6.4 Other Ionizing Gases in Water

Table 1-8 lists ionizing gases often found in cooling water systems:

TABLE 1-8
Ionizing Gases in Water

Gas	Source	Problems
Carbon dioxide	Air scrubbing, limestone rock	Calcium carbonate
Ammonia	Sewage water, air, processes	Microbiological fouling
Nitrogen oxides	Power plant emissions	Nitric acid corrosion
Hydrogen sulfide	Microbiological activity	Pitting corrosion
Sulfur dioxide	Power plant emissions	Sulfuric acid corrosion

Carbon dioxide is a natural component of water exposed to air. It may be considered an asset in some cooling water systems, or a contaminant in boiler feedwater (chapter 3). The other ionizing gases listed in Table 1-8 are generally introduced as contaminants. Table 1-8 shows the sources of these gases and problems that they cause. These problems are covered in more detail in chapters 3 and 4.

6.0 Carbonate Equilibria in Water

6.1 INTRODUCTION

The reactions of carbon dioxide in water, and the general subject of alkalinity, are extremely important concepts in water treatment. A correct understanding of these subjects is fundamental to all aspects of water pretreatment, cooling and boiler water treatment, and wastewater treatment.

For this reason, carbonate equilibria and alkalinity are discussed in detail in this section. Experienced water treatment professionals should review this material for reference purposes. New readers, on the other hand, may wish to skip the detailed chemistry and simply learn the alkalinity relationships in section 6.4.

6.2 REACTIONS OF CARBON DIOXIDE IN WATER

Carbon dioxide reacts with water in two stages:

- Carbon dioxide dissolves in water and reacts to produce carbonic acid:

$$CO_2\,(gas) + HOH \leftrightarrow CO_2\,(aq) \qquad (1\text{-}26)$$
$$CO_2\,(aq) + H_2O \leftrightarrow H_2CO_3 \qquad (1\text{-}27)$$

- Carbonic acid is a very weak acid (Table 1-5). Because it is a dibasic acid (contains two ionizable hydrogen atoms), it ionizes reversibly in two stages. The first stage produces bicarbonate ions:

$$H_2CO_3 \leftrightarrow HCO_3^- + H^+ \qquad (1\text{-}28)$$

- The second stage, ionization of bicarbonate, produces carbonate ions:

$$HCO_3^- \leftrightarrow CO_3^{-2} + H^+ \qquad (1\text{-}29)$$

Thus, the overall ionization of carbonic acid becomes the sum of equations (1-28) and (1-29):

$$H_2CO_3 \leftrightarrow CO_3^- + 2H^+ \qquad (1\text{-}30)$$

Because the bicarbonate and carbonate ions are both very weak acids (Table 1-5), they hydrolyze (react with water) to consume hydrogen ions as explained in section 4.3.5:

$$CO_3^{-2} + HOH \leftrightarrow HCO_3^- + OH^- \qquad (1\text{-}31)$$
$$HCO_3^- + HOH \leftrightarrow H_2CO_3 + OH^- \qquad (1\text{-}32)$$

Equations (1-31) and (1-32) are, in effect, the reverse of the ionization reactions (1-28) and (1-29).

It is easy to see from equations (1-26) through (1-32) that solutions of carbonate and bicarbonate in water become equilibrium mixtures of weak acids and bases. The net equilibrium in any solution of carbonate species in water is simply the sum of the individual reactions. Thus, equation (1-32), the hydrolysis of the bicarbonate ion, can be considered as the sum of three reactions: the ionization of the bicarbonate ion (equation 1-29); the ionization of water (equation 1-14); and the ionization of carbonic acid (equation 1-30):

$$HCO_3^- \leftrightarrow CO_3^{-2} + H^+ \qquad (1\text{-}29)$$

$$HOH \leftrightarrow H^+ + OH^- \qquad (1\text{-}14)$$

$$\underline{2H^+ + CO_3^{-2} \leftrightarrow H_2CO_3} \qquad (1\text{-}30A)$$

$$HCO_3^- + HOH \leftrightarrow H_2CO_3 + OH^- \qquad (1\text{-}32)$$

Equation (1-30A) is the same as equation (1-30), the overall ionization of carbonic acid, except that it is written in reverse order to show the arithmetic of adding equations more clearly; the equilibrium is the same. The actual concentrations of the ions in this solution will be determined by the equilibrium constants for all of the reactions involved.

6.3 CARBONATE SPECIES IN WATER vs pH

Remembering that pH is a measure of the hydrogen ion concentration in any solution, equations (1-28) through (1-32) show that the pH of any mixture of carbonate species will depend upon the relative amounts of carbonate, bicarbonate and unionized carbonic acid present. Carbon dioxide dissolved in pure water produces a solution of carbonic acid with a pH of about 4.0 (equations 1-26 through 1-29). At the other extreme, sodium carbonate (soda ash) in water produces a pH close to 9, from hydrolysis reaction (1-31).

This situation is not as complex as it might seem at first glance. The system can be easily understood from a plot of pH vs carbonate species, as shown in Figure 1-9.

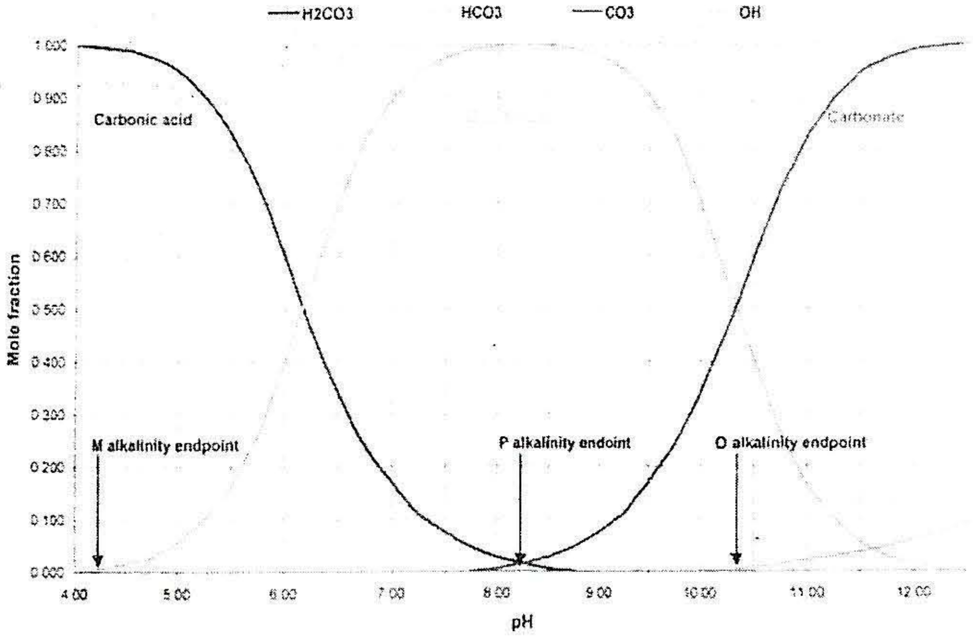


Figure 1-9. Effect of pH on carbonate species in water.

Consider a solution of carbon dioxide in demineralized water. The carbon dioxide will be reacted with water (hydrolyzed) to form carbonic acid (equation 1-27). Because carbonic acid is a weak acid, it will be only slightly ionized (equation 1-28), and the pH will be about 4.0. This corresponds to the data point at the top left corner of Figure 1-9.

Now consider slowly increasing the pH of this solution by adding a dilute solution of a strong base such as sodium hydroxide. This corresponds to moving to the right along the horizontal axis in Figure 1-9. As the pH increases, the added hydroxide ions react with the hydrogen ions from the carbonic acid (equation 1-28) to form water. This increases the ionization of carbonic acid to form more bicarbonate ions, needed to maintain the ionization constant for carbonic acid (Table 1-5). Thus, as the pH increases, the concentration of carbonic acid in the solution gradually decreases, and the concentration of bicarbonate (bottom left curve in Figure 1-9) increases.

This process continues, until at a pH of about 8.3, essentially all of the carbonic acid has been converted to bicarbonate ions. That is, the equilibrium in equation (1-28) has been shifted completely to the right by consuming the hydrogen ions with caustic. Another way to say this is that a dilute solution of sodium bicarbonate in pure water will have a pH of about 8.3.

This ionization process continues as the pH in Figure 1-9 increases beyond pH 8.3. Further additions of caustic cause the bicarbonate ion to ionize, to maintain the equilibrium shown in equation (1-29). When the pH in Figure 1-9 reaches about 12, all of the bicarbonate has been converted to carbonate.

Beginning at about pH 10, the hydroxide ion concentration in the water becomes important. Remember that the hydroxide ion concentration in the solution is controlled by the ionization constant for water (equation 1-16). At pH 10, the hydrogen ion concentration is very small ($[H^+] = 10^{-10}M$). To maintain the ionization constant for water at $K_w = 10^{-14}$, the hydroxide ion concentration must be $10^{-4}M$. This increases by factors of 10 as the pH increases.

This interpretation is somewhat simplistic, but it serves well for water treatment purposes. In fact, because of all the complex chemical equilibria involved (equations 1-16 and 1-29 through 1-32), the curves overlap somewhat. This overlap can be seen in Figure 1-9, at pH 8.3 and at pH 11.6. This overlap is ignored in normal water treatment calculations.

6.4 ALKALINITY

6.4.1 Definition

Early water chemists needed to know the amount of carbonate and bicarbonate in water supplies so that they could determine how much acid they needed to add to prevent calcium carbonate scale from forming. Mineral scale formation is discussed in section 7.

Water chemists defined the term "alkalinity" as the acid-neutralizing power of a water solution, referring to the bicarbonate, carbonate and hydroxide ions in the water. More precisely, this is called carbonate alkalinity. They measured alkalinity in field samples by titrating the water with 0.02N sulfuric acid, and they expressed their results as mg/L $CaCO_3$. The reason for this is a simple matter of convenience.

The molecular weight of sulfuric acid (H_2SO_4) is 98, and the equivalent weight is 49 (close enough to 50 for rough calculations). Fortuitously, the equivalent weight of calcium carbonate is also 50.

As explained in section 3.4.2, the general equation for titration calculations is:

$$\text{(ml titrant)} \times \text{(normality of titrant)} \times \text{(equiv. wt.)} = \text{mg.} \qquad (1\text{-}9)$$

In this case,

$$\text{(ml titrant)} \times 0.02 \times 50 = \text{(ml titrant)} \times 1 = \text{mg. } CaCO_3 \qquad (1\text{-}33)$$

Thus, a chemist can simply titrate a water sample with 0.02N sulfuric acid and read the burette directly as mg. alkalinity expressed as calcium carbonate. If his sample volume is 100 ml, he has only to multiply by 10 to calculate mg/L calcium carbonate.

6.4.2 Acid-Base Indicators

In addition to the total alkalinity in a water, it is important for cooling and boiler water treatment purposes to know the relative amounts of carbonate, bicarbonate and hydroxide ions present. This is also a simple matter of titration. In order to understand this titration, it is important to know how acid-base indicators work.

Indicators are organic compounds that exist in two different forms in water, depending on the pH. These two forms have different colors, and the transition between them occurs quickly over a narrow pH range. Table 1-9 lists a few of the common indicators used in water titrations:

TABLE 1-9
Indicator Solutions

Indicator	pH Range	Color change Acidic side	 Basic side
Bromophenol blue	3.0 - 4.6	Yellow	Blue
Methyl orange	3.2 - 4.4	Red	Yellow
Bromocresol green	3.8 - 5.4	Yellow	Blue
Ethyl red	4.0 - 5.8	Red	Yellow
Phenolphthalein	8.2 - 10.0	Colorless	Pink
Thymolphthalein	9.4 - 10.6	Colorless	Blue

For titrations with acid, the low pH end of the color change range, at which the color change appears to be complete, is taken as the end point of the titration.

Thus, when titrating with acid, using phenolphthalein as an indicator, the end point represents the last disappearance of pink color, at about pH 8.2.

6.4.3 M, P and O Alkalinity

To see how these indicators are used in alkalinity titrations, refer again to Figure 1-9. Consider a water solution containing sodium carbonate and sodium bicarbonate. The pH must be above 8, probably between 8.5 and 9. Add phenolphthalein indicator, and the solution will turn pink. Now begin titrating the solution with 0.02N sulfuric acid, as explained above. As acid is added, the pink color will gradually fade. The endpoint, when the color is gone, is the phenolphthalein end point. This is called the P alkalinity. It corresponds to the disappearance of carbonate from the solution (red curve in Figure 1-9), at a pH of 8.3.

Now, add bromocresol green indicator to the solution. The water will turn blue (see Table 1-9). Other indicators from Table 1-9 may also be used, with corresponding color changes. Continue the titration. At the end point, where the last bit of blue has faded to yellow, read the burette again. This is the M alkalinity point, at pH about 4.2. The letter M was chosen because methyl orange was the original indicator used for this titration. Figure 1-9 shows that at this point, all carbonate species have been neutralized to carbonic acid. Hence, M is also referred to as total alkalinity.

Figure 1-9 also shows an O alkalinity endpoint. This is the point above which the hydroxide ion concentration becomes significant in water treatment. Remember that the hydroxide ion concentration is controlled by the ionization of water, as shown in equation (1-16). There is no way to directly titrate O alkalinity, as there is with P and M alkalinity. O alkalinity is determined by calculation, as shown in section 6.4.4, below.

6.4.4 Alkalinity Calculations

At first glance, it would seem from Figure 1-9 that P alkalinity is equal to the carbonate ion concentration in the water. This is not correct. From equations (1-28) and (1-29), titrating the carbonate ion to zero at the phenolphthalein endpoint (Figure 1-9), simply converts the carbonate to bicarbonate ions. Another, equal amount of acid is needed to titrate the bicarbonate. Hence, the carbonate alkalinity in the water equals twice the measured P alkalinity.

There are two important factors to remember in alkalinity calculations:

1. All alkalinity values are expressed as calcium carbonate (section 6.3.1).
2. The total, or M alkalinity includes P alkalinity. This is one continuous titration with two indicators, first to determine P and then continuing with a second indicator to determine M.

TABLE 1-10
Alkalinity and Carbonate Species in Water

Alkalinity	Bicarbonate	Carbonate	Hydroxide
P = 0	M	0	0
2P < M	M – 2P	2P	0
2P = M	0	2P	0
2P > M	0	2(M – P)	2P – M

The following paragraphs illustrate and explain the alkalinity relationships in Table 1-10:

- If P = 0, that is, if phenolphthalein indicator does not turn red in the solution, Figure 1-9 shows that the only carbonate species in the water are bicarbonate and carbonic acid. Therefore, M = bicarbonate. Cooling waters with pH levels below about 8.3 fall into this category. (Note: if M also equals zero, then this is an acid solution containing only carbonic acid and possibly other mineral acids. See section 6.5 on acidity, below).
- If P is less than half of M, that is, 2P < M, then carbonate and bicarbonate are both present. The carbonate is equal to 2P as explained above, and the balance, or M - 2P, is bicarbonate. Cooling waters with pH above 8.3, and some low pH boiler waters, match this description.
- If P is equal to half of M, that is, 2P = M, then the carbonate alkalinity equals the total alkalinity and there can be no bicarbonate in the solution. This situation occurs only if there is no free caustic in the water (Figure 1-9).
- If P is greater than half of M, that is, 2P > M, then the excess over 2P, or 2P – M, must be caustic. In this case, then, the carbonate alkalinity equals the total minus the hydroxide, or M – (2P – M). This resolves to 2(M – P) as in Table 1-10.

Calculations based on these formulas are only approximate, but they can be very useful. In boiler water, for example, the hydroxide alkalinity, or O alkalinity, is calculated and controlled as 2P – M. In open cooling systems, the relative amounts of carbonate and bicarbonate present will be one factor in determining the degree of calcium carbonate scale protection required.

6.4.5 Alkalinity and pH

Equations (1-26) through (1-32) describe how the various carbonate species interact with each other and with water. Because of these interactions, systems with the same total (M) alkalinity can exist over a range of pH values.

As a simple illustration of this effect, consider a dilute solution of sodium carbonate (soda ash) in water. In this solution, 2P will equal M (Table 1-10) and the pH will be above 9. Now equilibrate this solution with air by rapid stirring for several hours, and then measure the pH and alkalinity. Carbon dioxide will have been absorbed from the air and reacted with carbonate to produce bicarbonate:

$$CO_3^{-2} + CO_2 + H_2O = 2HCO_3^- \qquad (1\text{-}34)$$

The P alkalinity will now be less than half of M, the pH will be down to perhaps 8.5, but the total M alkalinity will be unchanged. Carbonate ions have simply been replaced with an equivalent amount of bicarbonate ions, and the P/M ratio has changed.

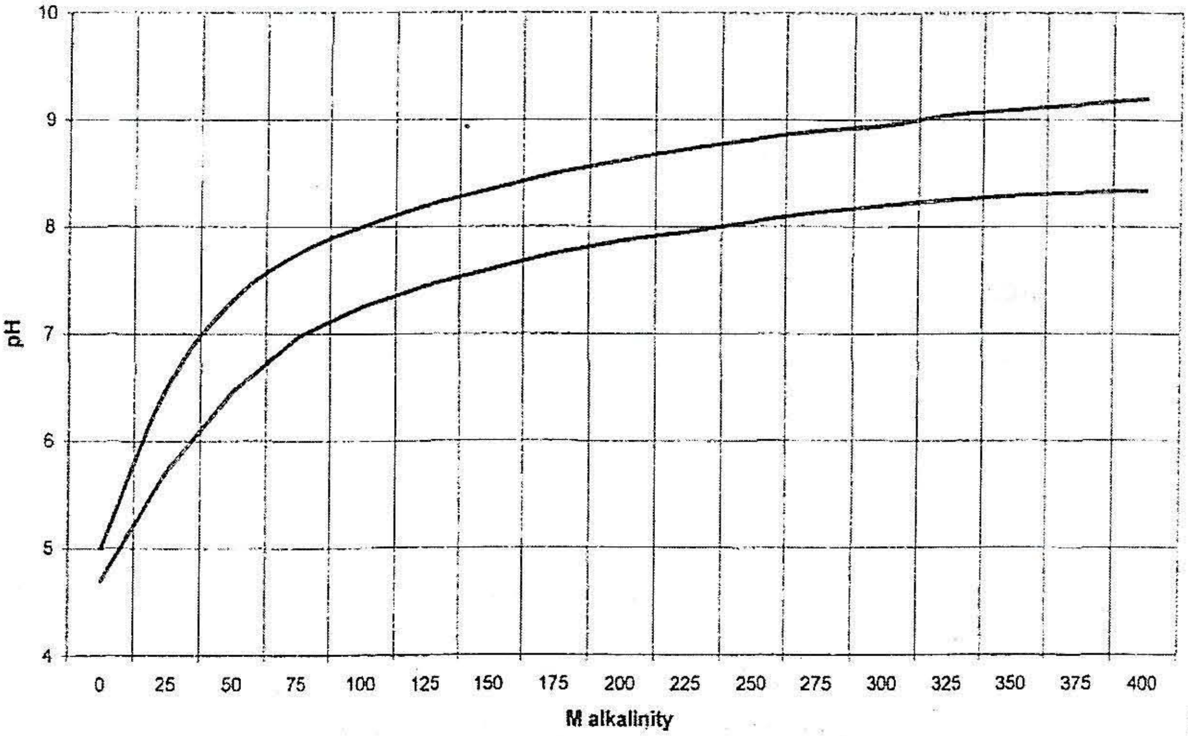


Figure 1-10. Alkalinity and pH relationships.

This relationship is shown in Figure 1-10. The graph shows that for any measured value of M, there can be a range of pH. The actual value depends upon the proportion of P alkalinity in the total (M). For this reason, M and P alkalinity provide a more precise description of the alkalinity relationships in an alkaline solution than does pH. Nevertheless, pH is widely used, because measurement and control are simple and reliable. See chapters 3 and 4 for information on the use of alkalinity data in boiler and cooling water treatment.

6.4.6 Noncarbonate Alkalinity

As explained in section 6.4.1, M and P relationships apply only to carbonate alkalinity. However, other ions in the water may be either acidic or basic, and may therefore affect an acid titration for alkalinity.

- For example, phosphates added to boiler and cooling water may be either acidic or basic. Often the phosphate levels are low compared to the alkalinity, so that the effect is small, but sometimes phosphates are a significant factor in total alkalinity. Phosphate chemistry is discussed in chapters 3 and 4 in this manual.

- Effluent wastewater used as cooling tower makeup may contain a substantial amount of both ammonia and phosphate. Acid titrations can still be used to determine acid requirements for pH control, but the alkalinity calculations in Table 1-10 will have no meaning.
- Any buffer chemicals added to a treatment program to help stabilize the pH, such as borate in closed systems, will make alkalinity calculations meaningless.

In these and other similar cases, it is very important to obtain complete water analyses and to interpret the data carefully. Water analyses are discussed further in section 10.

6.5 ACIDITY

Acidity, quite naturally, is the opposite of alkalinity. It represents the ability of a water solution to neutralize a base. Acidity is determined by titrating the water with dilute sodium hydroxide. As with alkalinity titrations, if the sodium hydroxide solution is 0.02N and the sample volume is 100 ml, acidity can be read directly from the burette as mg of calcium carbonate, and multiplied by 10 to yield mg/L.

6.5.1 Free Mineral Acidity (FMA)

Free mineral acidity, commonly known as FMA, represents compounds in the solution that produce hydrogen ions below pH 4.3.This is the methyl orange end point, below which M alkalinity is zero and all carbonate in the solution is in the form of carbon dioxide or unionized carbonic acid (see Figure 1-9). FMA is an important factor in ion exchange demineralization processes (chapter 2).

6.5.2 Total Acidity (TA) and Carbon Dioxide

Total acidity, or TA, is determined by continuing the titration after the FMA endpoint, to the phenolphthalein endpoint. Again from Figure 1-9, it can be seen that TA – FMA is a measure of the carbon dioxide content of the solution, expressed as calcium carbonate. It is important to know the carbon dioxide content of boiler feed water in order to calculate the required dosage of neutralizing amines in the condensate system (chapter 3).

If the P alkalinity in a solution is zero, so that no carbonate alkalinity exists (Figure 1-9 and Table 1-10), carbon dioxide can also be calculated from the pH and M values, as shown in Figure 1-11. To illustrate the use of Figure 1-11, if the pH is 7, the carbon dioxide to M ratio (CO_2/M) will be 0.12. Then, if M = 50 for example, the carbon dioxide content of the solution will be 50 x 0.12 = 6 mg/L, expressed as calcium carbonate.

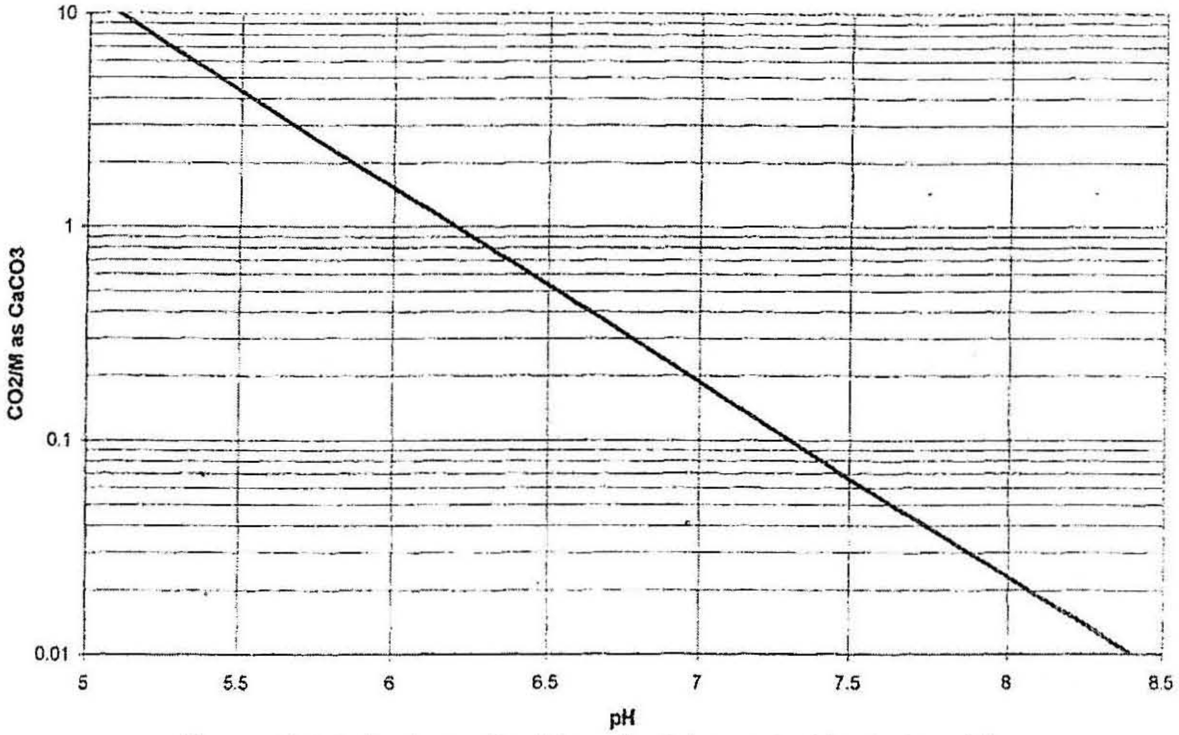


Figure 1-11. Carbon dioxide, alkalinity and pH relationships.

7.0 Mineral Scale Formation In Water

7.1 INTRODUCTION

Several different types of deposits can form in cooling and boiler water systems, and terms such as “scale”, “fouling”, “deposit”, “film”, “coating”, “precipitate” and others, are sometimes used interchangeably in the industry to describe these materials. It is important to be precise about this, because the operating procedures and chemical treatments used to help prevent these various deposits from forming, and to remove them when necessary, depend upon the specific composition of the deposits. Terms are therefore defined in this section and in subsequent sections of this chapter as they are used, and these definitions are used consistently throughout the manual.

- Deposit is a general term referring to any material formed on either the internal or external surfaces of metal components in contact with water.
- Fouling is also a general term used to describe the condition of a system in which deposits have formed.
- Mineral scale refers specifically to deposits formed by precipitation of inorganic salts from solution. Thus, mineral scale does not include corrosion products, microbiological deposits or deposits of suspended solids from water. These are covered in subsequent sections in this chapter, and in chapters 3 and 4.

Most of the common inorganic compounds found in water systems are at least moderately soluble in water below a pH of about 7. Some of these compounds, notably calcium carbonate and calcium phosphate, become only slightly soluble, and therefore tend to precipitate in the alkaline pH range. Historically, the use of acid to control the pH of the solution below 7 was the only practical way to prevent mineral scale formation in open cooling systems.

Acid feed is still used for mineral scale control, especially in large industrial and power station cooling systems. However, In the years since about 1980, environmental and safety regulations have made acid feed a less viable option, and many cooling systems now operate without pH control. To make matters worse, common mineral scales, such as calcium carbonate and calcium phosphate, are inversely soluble (section 5.4), so that they precipitate preferentially on heat transfer surfaces.

Mineral scales can severely limit heat transfer efficiency. It has been shown that as little as 1/16 inch of calcium carbonate on a condenser tube can lead to a 50 percent loss in cooling capacity. Thus, mineral scale control has become a major part of modern cooling water treatment. This section discusses the basic chemistry involved in mineral scale control. Scale control technology is covered in detail in chapter 4.

7.2 CALCIUM CARBONATE

Calcium carbonate is by far the most common mineral scale. It appears in municipal water supplies, all kinds of cooling systems, boilers that do not use softened or demineralized water (see chapter 2) and many process water systems.

7.2.1 Solubility and Crystallization

Calcium carbonate is inversely soluble, so that it precipitates preferentially as scale on heated surfaces such as the bottoms of tea kettles and the water side surfaces of boiler and heat exchanger tubes. In cooling water condenser tubes, it forms as a smooth, light tan to brown, egg shell-like deposit. Pure calcium carbonate is white. The color results from the inclusion of iron oxides, dirt and other impurities in the scale. Calcium carbonate also forms in cooling systems as a loose slurry of crystals mixed with other debris in the basin, and as deposits on walls, fill, etc.

Calcium carbonate, and other minerals, tend to form supersaturated solutions. That is, even though the concentration of calcium carbonate in a given solution may be higher than the equilibrium value calculated from the solubility product, scale may not precipitate immediately. Crystal formation may depend upon the presence of "seed" crystals of calcium carbonate or another substance with a similar crystal habit. Thus, one method of controlling calcium carbonate and other mineral scales is to extend the stability of supersaturated solutions. See section 7.5, below, and chapter 4 for more on this subject.

Calcium carbonate can exist in three different crystalline forms, or "habits". Each is stable under different temperature and pH conditions. The stable form under most cooling tower conditions is calcite. Some cooling water additives, especially synthetic organic polymers and phosphonates, have the ability to modify crystal structures as they form. This makes the crystals unstable, and is therefore another useful method for preventing calcium carbonate scale formation. See chapter 4 for more on this important subject.

7.2.2 Hardness

Hardness is a historical term used to describe the hard calcium and magnesium carbonate scales found in improperly treated boilers and cooling water systems. Water was "softened" by removing the hardness elements, calcium and magnesium, from the water. Softening is discussed in chapter 2.

Early water treaters found that they could remove some, but not necessarily all of the hardness ions from water by boiling. Boiling converts bicarbonate alkalinity to carbonate, and precipitates an equivalent amount of calcium and magnesium as carbonate salts. The amount of calcium and magnesium equivalent to the alkalinity in a solution is called the temporary hardness. The excess calcium and magnesium, if any, that cannot be removed in this way, is called the permanent hardness.

Calcium and magnesium hardness values are both <u>always</u> expressed as calcium carbonate, so that they can be calculated together (section 3.4.3). Laboratories sometimes report alkalinity and hardness as calcium carbonate, and individual ions as the ions. This can lead to confusion unless the appropriate corrections are made. The following conversion factors are used:

$$Ca^{+2} \times 2.5 = CaCO_3 \qquad (1\text{-}35)$$

$$Mg^{+2} \times 4.1 = CaCO_3 \qquad (1\text{-}36)$$

Laboratories can easily determine calcium and magnesium levels by instrumental methods. In the field, it is easy to determine total hardness by a titration method that includes both calcium and magnesium. If it is necessary to determine calcium and magnesium separately in the field, total hardness and calcium are titrated separately as calcium carbonate, and magnesium is determined by difference. Analytical methods are not discussed in this manual. For more information, refer to the references at the end of this chapter.

7.3 THE LANGELIER STABILITY INDEX (LSI)

Obviously, the solubility of calcium carbonate in a given system depends upon the carbonate equilibria in that system, as defined by the alkalinity (section 6). Since alkalinity can be easily titrated, it is possible to use alkalinity, calcium and pH data, together with temperature, to predict calcium carbonate solubility. This, in turn, allows water treaters to design calcium carbonate scale control programs to match field conditions.

7.3.1 Development of the LSI

Municipal water authorities often depend upon formation of a thin film of calcium carbonate scale on their system piping to provide a degree of corrosion protection. This requires adjusting the water chemistry, usually with lime or soda ash, to allow some scale to form, and then, after some time, readjusting the chemistry to stabilize the system and prevent further scale formation.

For this purpose, a stable water is defined as a water that will neither precipitate nor dissolve calcium carbonate on standing. The marble test is a simple way to qualitatively measure the stability of a water. A small amount of ground marble chips is added to a beaker of the test water, and the beaker is allowed to stand for several hours. The chips act as a seed for precipitation. If a cloud of white floc appears on the chips, the water is supersaturated and calcium carbonate is precipitating. Alternatively, if small bubbles appear on the chips, the water is undersaturated and is dissolving the chips, liberating carbon dioxide gas.

In 1936, Prof. W. F. Langelier developed an empirical, but quantitative method for calculating the stability of a water solution. He defined a function, pH_s, as the pH of saturation for calcium carbonate in any given water. pH_s is a function of calcium and alkalinity, both expressed as calcium carbonate, plus the temperature and conductivity of the water. Conductivity is a measure of the total ionic strength of the water. In high conductivity waters, interionic reactions tend to increase the solubility of calcium carbonate and other minerals.

Having defined pH_s, Langelier further defined the Langelier Stability Index (LSI) as the difference between the actual pH of a water and the pH_s. That is:

$$LSI = pH - pH_s \tag{1-37}$$

If the actual pH is higher than pH_s, the LSI is positive and calcium carbonate will precipitate. If the actual pH is lower than pH_s, the LSI is negative and calcium carbonate will dissolve.

7.3.2 LSI Calculations

Langelier's equations for calculating pH_s have been modified over the years. The actual equations are cumbersome and are rarely used. pH_s is now easily determined from readily available Tables, nomographs and slide rules.

Also, sophisticated computer programs are available that calculate pH_s from fundamental solubility equilibria, rather than from Langelier's empirical equation. These programs take into account expected ionic interactions that can affect solubility, and are therefore more accurate than the empirical calculation. Computer-generated values of pH_s are generally 0.2 to 0.3 units lower than the empirical values. For rough estimates of the scaling tendency of a water, these differences are normally not significant, and calculations based on slide rules or Tables are sufficient.

7.3.3 Proper Use of the LSI

Use of the LSI as a guide to selecting calcium carbonate scale control methods is covered in chapter 4. Following are some general principles that apply to all applications of the LSI:

- Because the LSI was originally developed as a guide for corrosion control in municipal water systems, Langelier designated positive values of the LSI as scaling, and negative values as corrosive. This terminology has carried through to modern times. It is, however, a misnomer. In fact, the LSI does not in any way predict the corrosivity of a water supply. Waters with positive LSI values can still be corrosive to steel and other metals. Modern scale control technology, that can completely eliminate calcium carbonate scale in a positive LSI system, may, by doing so, create a severe corrosion problem. Corrosion theory is discussed in section 8.0, below, and corrosion control technology is covered in chapters 3 and 4.
- Municipal water distribution systems do not involve heat transfer, so that temperature differences were not considered in the original development of the LSI. When applied to open cooling water systems, however, temperature is a significant variable. Because of the inverse solubility of

calcium carbonate, an LSI calculation that is negative at the basin water temperature may be strongly positive (scaling) at the condenser water outlet temperature, or, even more important, at the skin temperature of the condenser tubes (see section 2.3.2). Always calculate the LSI at the highest water temperature in the system, and for best reliability, add another 10 to 20 °F to account for skin temperature.

- The LSI is most reliable under average operating conditions. It loses sensitivity in high pH and high conductivity systems. LSI values above about +2.5 should not be considered reliable. Under these conditions, computer-generated LSI values are more useful. See also section 7.3.4 on alternative scaling indices.
- Finally, the LSI is an equilibrium calculation. It does not take into account supersaturation, rate of precipitation, effects of flow velocity in condenser tubes, and other physical factors that can influence mineral scale formation. For these reasons, the LSI should be used only as a guide, not as a quantitative predictor of calcium carbonate scale formation.

7.3.4 Other Scaling Indices

The Ryznar Index. In 1944, Dr. John Ryznar noted that the LSI did not correlate well with field results in high pH lime-softened municipal water supplies. Ryznar developed an alternative system, derived from the LSI. He defined the Ryznar Index (RI) as equal to twice the pH_s minus the actual pH of the system. That is:

$$RI = 2pH_s - pH \qquad (1\text{-}38)$$

In this system, an RI value of +6 corresponds to a stable water with an LSI value of 0. Over the range of normal cooling water operations, the RI and LSI provide roughly equivalent data. Neither should be trusted under extreme scaling conditions. The LSI is the more fundamental function and is more easily calculated, and for those reasons is more frequently used.

The Puckorius Index. The Puckorius Index is a further refinement of the Ryznar Index, in which an empirical alkalinity function derived from Figure 1-9 is used to modify the calculated pH_s. In large industrial and power station cooling systems, either the LSI or the Puckorius Index is sometimes used to control acid feed for calcium carbonate scale control. See chapter 4 for more on this subject.

Saturation Ratios. With the aid of computer databases of solubility information, it is possible to calculate equilibrium equations that take into account all of the ionic interactions that occur in high ionic strength solutions. One of these equations is the saturation ratio (SR), calculated as the ratio of the ionic concentrations to the equilibrium solubility product. For calcium carbonate:

$$SR = [Ca^{+2}][CO_3^{-2}]/K_{sp}CaCO_3 \qquad (1\text{-}39)$$

In performing this calculation, the computer program uses not the analytical concentrations of calcium and carbonate ions, but calculated values that take into account portions of the calcium and carbonate that are tied up in other ionic interactions and are therefore not available to precipitate as calcium carbonate. SR data calculated in this way are more reliable than even LSI data calculated from the same computer database.

7.4 OTHER MINERAL SCALES

It is important to remember that the LSI and RI calculations apply only to calcium carbonate scale. Other mineral scales important in cooling water systems include calcium phosphate, calcium sulfate, silica and magnesium silicate. A pH_s calculation for calcium phosphate is available, but it has little value because of the complex precipitation chemistry of calcium phosphate and its tendency to form stable supersaturated solutions that precipitate slowly.

However, computer-generated saturation ratios for other mineral scales, calculated in the same way as equation (1-39), are helpful in predicting water treatment requirements. "Rules of thumb" for the solubilities of calcium sulfate, silica and magnesium silicate are also useful. Mineral scale control in cooling water systems is discussed in detail in chapter 4 in this Manual.

8.0 CORROSION OF METALS IN WATER

8.1 INTRODUCTION

Corrosion is defined, in general terms, as damage caused to a material by reaction with its environment. In this context, materials include metals, nonmetals, even natural materials such as wood. Environments include air (oxygen) and other gases, for example ammonia, hydrogen sulfide and exhaust gases; water and other fluids such as refinery process streams; and temperatures from subarctic to over 1000 °F in petrochemical plants.

Another way to consider corrosion is as the tendency of any material to return to its natural state by reacting with its environment. Most of the reactive elements in the periodic table exist in nature as compounds. These may be oxides, such as ferric oxide (Fe_2O_3) in iron ore, simple salts such as sodium chloride (NaCl), or a wide variety of more complex inorganic and organic compounds. Work and energy, as in a steel mill, are required to convert ferric oxide to metallic iron that can then be blended with carbon and other elements to make steel. This is akin to pushing a ball uphill. The second law of thermodynamics states that all naturally occurring reactions involve a release of energy. Thus, iron tends to release energy as it returns to rust (Fe_2O_3), just as the ball releases energy as it rolls back downhill.

This section discusses basic corrosion mechanisms for iron (steel) in water. Specific corrosion and corrosion control technology related to boiler and cooling water systems is covered in chapters 3 and 4.

8.2 BASIC ELECTROCHEMISTRY

Readers may wish to review section 3 (basic chemistry) as preparation for reading this section on electrochemistry. Beginning readers may wish to skip this section, and return later for reference after studying chapter 4.

8.2.1 Oxidation-Reduction (Redox) Reactions

The chemical reactions discussed so far in this chapter do not involve any change in the valence of the reacting ions or compounds. Thus, when calcium and carbonate ions react in water to produce precipitated calcium carbonate scale, none of the ions involve a change in valence:

$$Ca^{+2} + CO_3^{-2} = CaCO_3\downarrow \qquad (1\text{-}40)$$

In equation (1-40), the down arrow means that the compound is insoluble and precipitates from the solution. Similarly, in other reactions, an up arrow means that the compound is a gas that escapes from the solution.

In another class of reactions, called electrochemical reactions, electrons are transferred from one element or ion to another, and a change in valence state is involved. Thus, when iron reacts with dissolved oxygen in water, iron loses two electrons and is <u>oxidized</u> to ferrous iron, while oxygen loses two electrons and is <u>reduced</u> to hydroxide ions in water:

$$2Fe + O_2 + 2H_2O = 2Fe^{+2} + 4OH^- \qquad (1\text{-}41)$$

In equation (1-41), the valence of iron changes from 0 to +2, releasing two electrons, and the valence of oxygen changes from 0 to –2, consuming two electrons. (Valence and ionization are discussed in section 3.3). This is an electrochemical reaction, because it involves a transfer of electrons. It is also called a redox reaction, because one component of the reaction is oxidized and another is reduced.

All electrochemical reactions can be separated into two half-reactions:

1. An oxidation reaction in which an element is oxidized and electrons are released:

$$2Fe^0 = 2Fe^{+2} + 4e^- \qquad (1\text{-}41A)$$

2. A reduction reaction in which these electrons are consumed:

$$O_2 + 2H_2O + 4e^- = 4OH^- \qquad (1\text{-}41B)$$

The sum of these two half reactions is the overall corrosion reaction for iron in water, equation (1-41). Note that the four electrons generated in equation (1-41A) are consumed in equation (1-41B) to maintain electrical neutrality.

To complete the process, the ferrous iron and hydroxide ions in equation (1-41) combine to produce black ferrous hydroxide:

$$2Fe^{+2} + 4OH^- = 2Fe(OH)_2\downarrow \qquad (1\text{-}41C)$$

If sufficient dissolved oxygen is present in the water, black ferrous hydroxide is oxidized further to red ferric hydroxide:

$$4Fe(OH)_2 + O_2 + 2H_2O = 4Fe(OH)_3\downarrow \qquad (1\text{-}42)$$

This redox reaction, just like equation (1-41), can be split into two oxidation and reduction half-reactions:

$$4Fe^{+2} = 4Fe^{+3} + 4e^- \qquad (1\text{-}42A)$$

$$8OH^- + O_2 + 2H_2O + 4e^- = 12OH^- \qquad (1\text{-}42B)$$

Over time, ferric hydroxide dehydrates (loses water) to become the familiar brown ferric oxide corrosion product, rust:

$$4Fe(OH)_3 = 2Fe_2O_3 + 6H_2O \qquad (1\text{-}43)$$

Mixtures of ferric hydroxide and ferric oxide from equations (1-42) and (1-43) make up the familiar corrosion product found in cooling water piping systems. Black ferrous hydroxide (equation 1-41C) is often found next to corroding metal, beneath ferric oxides and hydroxides, where water circulation may be poor and dissolved oxygen levels inadequate for complete reaction .

8.2.2 Oxidizing and Reducing Agents

In general terms, oxidation involves raising an element or ion to a higher valence state by removing electrons. Thus, in the corrosion reaction on steel (1-41A), zero valence iron metal is oxidized to ferrous ions by removing two electrons. The oxidizing agent, in this case oxygen, accepts these electrons and is, itself, reduced (equation 41B).

Typical oxidizing agents in water systems include dissolved oxygen and hydrogen ions (acid). The redox reaction of hydrogen, as part of the corrosion of steel in acid systems, is discussed in section 8.3.1, equation (1-44).

Said conversely, the corroding metal in a corrosion reaction is a reducing agent. It reduces the corrodant, dissolved oxygen or hydrogen ions, by donating electrons, and is, itself, oxidized. Oxygen scavengers, such as sulfite and hydrazine, that remove dissolved oxygen in boiler water, are reducing agents (see chapter 3).

Some corrosion inhibitors, such as nitrite and chromate (see chapter 4) are oxidizing and passivating agents. They directly corrode metal surfaces to form adherent, passive films (see section 8.3.2, below). Oxidizing biocides, such as chlorine, bromine, chlorine dioxide, hydrogen peroxide and ozone, act by removing electrons to change or destroy organic matter. These compounds can also take part in cathodic reactions on steel to increase corrosion rates. All of these concepts are discussed in detail in chapter 4.

8.2.3 Anodes, Cathodes and Electrical Neutrality

As explained in section 3.3, it is a basic principle of all chemical reactions in nature that electrical neutrality must be preserved. Note that in equations (1-40) through (1-43), either there are equal numbers of positive and negative charges on one side of the equation, or there are equal numbers of the same charge on both sides of the equation, so that they cancel each other. In both cases, the overall reactions are neutral. If this were not the case – that is, if electrical neutrality were not preserved – a current would flow through a circuit to balance the charges. This is the basis for all chemical batteries, and it is the driving force for electrochemical corrosion reactions.

Consider now a clean metal surface, e.g. a new steel corrosion coupon, in a water system. As long as current flow is possible and electrical neutrality is preserved, the metal surface will corrode. Figure 1-12 is a schematic drawing of a typical corrosion cell on steel in water.

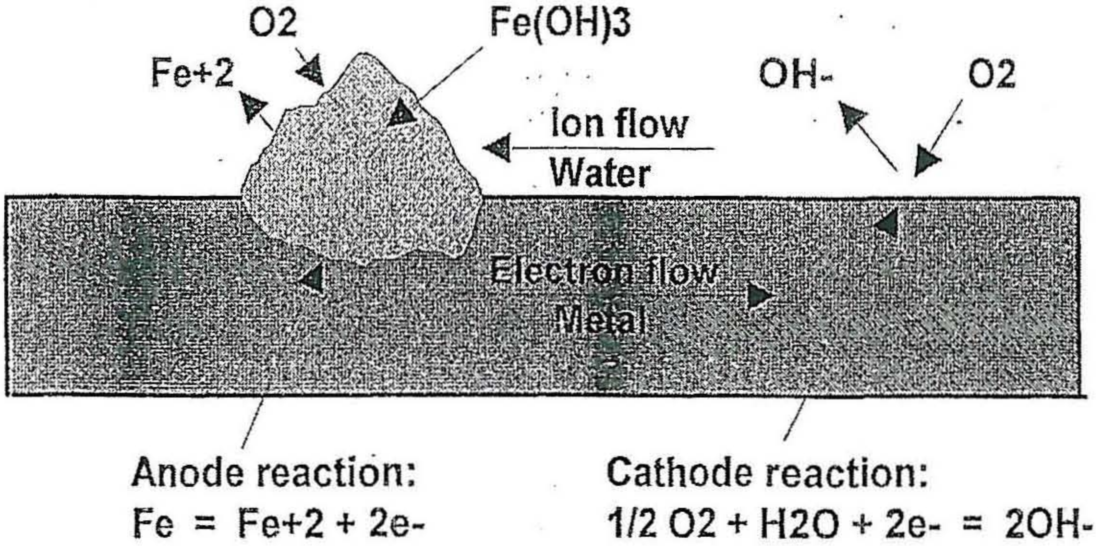


Figure 1-12. Simplified corrosion cell for iron in water.

On a microscopic level, the metal surface is not perfectly uniform. Corrosion will begin at points that are metallurgically more stressed (active) due to manufacturing and surface treatment. The points at which corrosion occurs and iron is lost to the solution are called anodes, and the oxidative half-reaction at that point (equation 1-41A) is called the anodic reaction, as shown in Figure 1-12. Similarly, the complementing half-reaction, the reduction of oxygen (equation 1-41B) occurs at less active points on the surface, called cathodes.

As shown in Figure 1-12, electrons generated at the anodic sites flow through the metal to the cathodic sites, where they are consumed by the cathodic reaction. To maintain electrical neutrality, negative hydroxide ions generated at the cathodic sites by the reduction of dissolved oxygen flow back through the water to the anodic sites, completing the electrical circuit. At the anodes, the hydroxide ions react with newly dissolved iron to form ferrous and ferric hydroxides, as shown in equations (1-41C) and (1-42).

If the metal surface is generally uniform and clean, the anodic and cathodic sites will be microscopically close together and may shift around the surface over time. The result is general surface corrosion. However, if the surface is not uniform, anodes and cathodes may remain separated, leading to localized corrosion as shown in Figure 1-12. There are many different forms of localized corrosion that can cause severe damage in cooling and boiler systems. Localized corrosion is discussed in detail in chapter 4.

8.3 FACTORS AFFECTING CORROSION RATES IN WATER

8.31 Effect of pH on Corrosion

Figure 1-13 shows a generalized corrosion rate curve for low carbon steel in soft water. The rate is relatively flat at about 9-10 mpy in the pH range from about 4 to 10. This is the pH range in which carbon dioxide (carbonic acid) and its ionization products, bicarbonate and carbonate ions (section 6), control the pH.

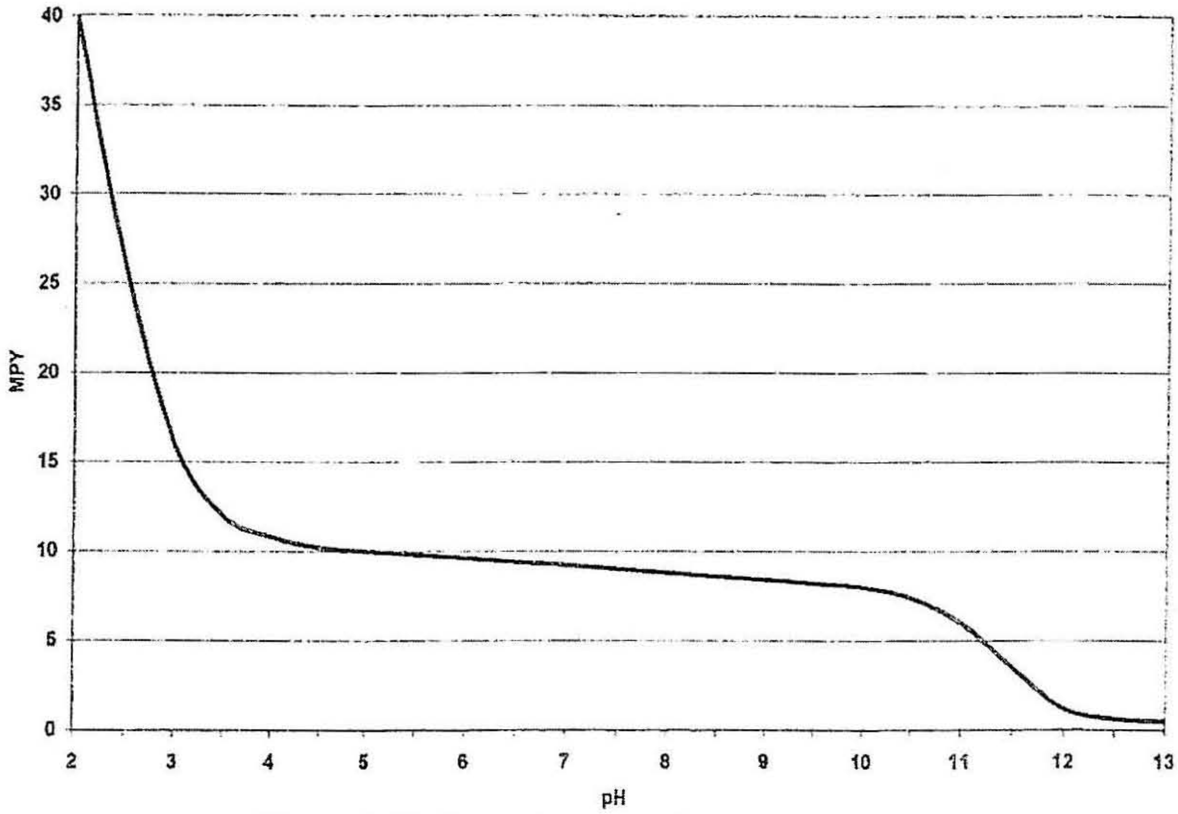


Figure 1-13. Corrosion rate of carbon steel in soft water.

Below pH 4.3, the total (M) alkalinity of the water is zero, and free mineral acidity (FMA) controls the pH. The cathodic corrosion reaction changes from the reduction of oxygen to hydroxide ions (equation 1-41B) to the reduction of hydrogen ions to form hydrogen gas:

$$2H^+ + 2e^- = H_2\uparrow \qquad (1\text{-}44)$$

Thus, a steel coupon immersed in a solution of 0.01N hydrochloric or sulfuric acid (pH = 2) quickly becomes covered with bubbles of hydrogen gas as the metal dissolves.

Above pH 10, the hydroxide ion concentration in the water becomes significant (see section 6.4.3 and Figure 1-9). The increasing concentration of hydroxide ions tends to shield the cathodic areas where hydroxide ions are generated.

As a result, the cathodic half-reaction (equation 1-41B) and thus the overall corrosion rate are reduced as shown in Figure 1-13. This process is called polarization (see section 8.3.3). Above pH 13, the corrosion rate of steel in water increases again, because the corrosion product, ferric hydroxide, begins to redissolve to form soluble ferrate ions.

8.3.2 Other Factors that Influence Corrosion Rates in Water

In real systems, the corrosion rate curve in Figure 1-13 is influenced by the dissolved solids content (conductivity), temperature, hardness and alkalinity of the water:

- Increasing the dissolved ionic solids in the water increases the conductivity and thereby increases the corrosion rate, by allowing more corrosion current to flow (Figure 1-12). This, however, is not a linear relationship. Divalent and trivalent ions carry proportionally more current than do monovalent ions, because of their higher charges. As a general rule-of-thumb, the dissolved ionic solids level in a solution, in mg/L, can be assumed to be between about 65 and 75 percent of the measured conductivity.
- Temperature increases the rates of most chemical reactions. Increasing temperature increases the negative electrode potentials of reactive metals, and also increases the diffusion rate of dissolved oxygen in water. The result is another general rule-of-thumb: corrosion rates in water solutions tend to double for every 10 to 15 °C (18 to 27 °F) increase in temperature.
- Increasing hardness and alkalinity reduce corrosion rates by increasing the tendency of the water to form protective calcium carbonate films. See the following section 8.3.3 for more on this subject.

8.3.3 Polarization and Cathodic Control

Because electrical neutrality must be preserved, any process that interferes with either the anodic or cathodic half-reaction in a corrosion process will necessarily reduce the rate of the other reaction, and thereby reduce the overall corrosion rate. For this reason, most corrosion reactions are self-limiting. Products of the corrosion half-reactions accumulate at the metal surface and tend to shield the surface.

Hydroxide ions generated at cathodic sites (equation 1-41B) adsorb at the cathodes and interfere with the ability of dissolved oxygen to reach the active surface. Also, hydroxide ions react with bicarbonate alkalinity to form carbonate:

$$HCO_3^- + OH^- \leftrightarrow CO_3^{-2} + H_2O \qquad (1\text{-}45)$$

Carbonate ions, in turn, react with calcium to precipitate calcium carbonate as a film at the metal surface. This film further shields the cathode and reduces the cathodic corrosion rate.

In low pH systems, where reduction of hydrogen ions is the dominant cathodic reaction, micro bubbles of hydrogen form at the cathodes and, in the same way, interfere with the flow of new hydrogen ions to the surface.

These processes and others that occur on corroding metal surfaces are forms of a process called polarization. Products of corrosion reactions, and other natural processes that form films on corroding surfaces, polarize the surface and reduce the corrosion rate by slowing the half-reaction at that surface.

Polarization is influenced by operating variables. High temperatures cause films to become less stable and disperse. High velocity can sweep away adsorbed films. Low pH water can dissolve corrosion products and other polarizing films. This process is called depolarization.

Polarization processes at the cathodic areas in a corroding system reduce the rate at which dissolved oxygen can reach the metal surface. The corrosion rate in such systems is said to be under cathodic control, and the controlling factor is the diffusion rate of dissolved oxygen to the metal surface.

Anodic polarization can also occur, usually by corrosion products that accumulate at anodic sites. However, the anodic reaction – dissolution of metal, as shown in equation (1-41A) – does not depend on surface reactions, as does the cathodic reaction. Hence, anodic polarization does not reduce the corrosion rate, even though the available anodic area may be reduced. Since the overall rate is under cathodic control, this effect can lead to concentration of the anodic corrosion rate in small areas, causing deep penetration or pitting of the surface. This effect is discussed further in chapter 4.

Polarization is a dynamic phenomenon. The process can be changed or reversed by changing system conditions. Thus, for example, very high water flow velocities can prevent polarization of cathodic surfaces and thereby increase corrosion rates. The concepts of polarization, and cathodic control are very important in materials selection and water treatment for corrosion control. These concepts are discussed in detail in chapter 4.

8.4 THE GALVANIC SERIES

So far, the discussion of electrochemistry and corrosion in this section has been confined to the corrosion of iron (steel) in water. Of course, many other metals corrode in water, some much more actively than iron, some less so. Still other metals do not corrode in water.

Scientists have devised a method of comparing the activities of metals by measuring the electrode potentials for the oxidative half-reactions, e.g. equation (1-41A), relative to a standard electrode. The standard chosen for this purpose is the hydrogen electrode, corresponding to the half-reaction for the oxidation of hydrogen to hydrogen ions:

$$H_2^0 \rightarrow 2H^+ + 2e^- \qquad (1\text{-}46)$$

Table 1-11 lists some common metals in order of their electrode potentials, along with the electrochemical half-reactions corresponding to dissolution of the metal (corrosion). This is called the electrochemical series. The most active metals, that react most easily in water, are at the top of the Table, and the noble metals, that do not corrode in water, are at the bottom.

TABLE 1- 11
The Electrochemical Series of Metals

Metal	Half-reaction	Electrode potential volts vs. std. H2 elect.
Active (anodic)		
Potassium	$K = K^+ + e^-$	-2.93
Calcium	$Ca = Ca^{+2} + 2e^-$	-2.87
Sodium	$Na = Na^+ + e^-$	-2.71
Magnesium	$Mg = Mg^{+2} + 2e^-$	-2.37
Aluminum	$Al = Al^{+3} + 3e^-$	-1.66
Zinc	$Zn = Zn^{+2} + 2e^-$	-0.76
Iron	$Fe = Al^{+3} + 3e^-$	-0.44
Nickel	$Ni = Ni^{+2} + 2e^-$	-0.25
Tin	$Sn = Sn^{+2} + 2e^-$	-0.14
Lead	$Pb = Pb^{+2} + 2e^-$	-0.13
Hydrogen	$H_2 = 2H^+ + 2e^-$	0.00
Copper	$Cu = Cu^{+2} + 2e^-$	0.34
Mercury	$Hg = Hg^{+2} + 2e^-$	0.79
Silver	Ag = Ag+ + e-	0.80
Gold	$Au = Au^{+3} + 3e^-$	1.50
Noble (cathodic)		

Table 1-11 is selected from a much larger Table of electrochemical half-reactions that includes oxidation and reduction reactions for most of the elements in the periodic Table.

Tables similar to Table 1-11 can be prepared with a different half-reaction chosen as the arbitrary standard, e.g. the mercury calomel cell. Also, half-reactions can be measured in special environments such as sea water. A practical series of half-reactions in sea water, called a galvanic series, is discussed in chapter 4 as a way to predict potential corrosion by dissimilar metals in contact. This effect, called galvanic corrosion, is discussed in the following section.

8.4.1 Galvanic Corrosion

When two metals from Table 1-11 are coupled together, for example, if a steel nipple is screwed directly into a copper fitting, the potential difference between the two metals, as shown in the Table, constitutes the driving force for an electrochemical reaction. This is called galvanic corrosion. The more noble metal, in this case copper, becomes the cathode, where reduction of oxygen occurs (equation 1-41B). The active metal, in this case iron, becomes the anode (equation 1-41A), and the steel threads in contact with the copper fitting corrode rapidly.

The potential difference between copper and zinc or aluminum is even greater than between copper and iron. Galvanized steel or aluminum in contact with copper in water can be damaged very quickly by galvanic corrosion. Galvanic corrosion is a serious problem in water treatment that is discussed in more detail in chapter 4.

8.4.2 Passivation

The elements at the top of Table 1-11, potassium, calcium and sodium, are so active that they cannot exist as metals in contact with water. They react explosively with water to produce hydroxide ions and hydrogen gas. For example:

$$2Na + 2H_2O \rightarrow 2Na^+ + 2OH^- + H_2\uparrow \qquad (1\text{-}47)$$

The next two elements in Table 1-9, aluminum and zinc, also have very active potentials, but they can exist for long periods of time in contact with water without any visible reaction. The difference is that aluminum and zinc form stable protective oxide coatings in air that protect the metal from contact with oxygen in air and in water.

This process, called passivation, is similar to polarization (section 8.3.3). It involves natural formation of so-called "permanent" protective films on metal. These films are usually oxides that are inert under a range of operating conditions. Galvanized steel (zinc), stainless steels, and aluminum are examples of metals that form stable passive oxide films and thereby provide good corrosion protection in water systems. Passivation is also discussed more fully in chapter 4.

9.0 SYSTEM SURVEYS

9.1 KNOWLEDGE OF FACILITY OPERATIONS

The sections in chapter 1, up to this point, have been concerned with the basic chemical knowledge needed to understand both corrosion and mineral scaling problems in water systems. The technology to manage these problems successfully is explained in the following chapters.

The need for all the technical information in this manual becomes clear when it is time to plan, install and service a water treatment program in a new customer account. However, knowledge of water supplies and water treatment technology alone is not sufficient. In order to do a good job, a water treatment professional must know and understand his/her customer's operations. There are two parts to this knowledge:

- General process knowledge
- Specific customer plant knowledge

9.1.1 General Process Knowledge

Understanding, in a general way, how HVAC systems work, how steel and paper and textiles are made, and how electric utility stations operate, make it possible to "talk the customer's language". Facility personnel appreciate a water treatment professional who understands process systems and terminology, and is able to interpret properly the information he/she receives about operations and problems.

For example, referring to HVAC systems, it is important to understand what a building engineer means when he reports that he has "head loss problems", or that his "secondary chilled water is an injection system." This understanding makes it possible to communicate with the engineers and use water treatment knowledge to recognize and solve problems in these systems.

As stated earlier, process technology is beyond the scope of this manual. Many available textbooks, technical papers and operating manuals contain this information. Some of these are listed as references at the end of this chapter.

9.1.2 Applying Water Treatment Knowledge

Never assume that two industrial plants, power stations or commercial HVAC systems are alike, just because they are close together and use the same water supply. Each facility is unique in the way it is built and operated.

Following are just a few examples of factors in apparently similar plants that can create a weak link and destroy a chemical treatment program:

- Two parallel heat exchangers may appear to be identical, but one may be larger than the other. The operators may have to throttle water flow through the larger unit to maintain a process temperature, while the smaller exchanger may be able to run at full flow. The larger exchanger will be much more likely to develop deposit and corrosion problems. This may be the critical unit that defines the water treatment program required in this plant.

- Two commercial office buildings may be constructed as "twins", but one may contain bank trading floors that must operate continuously, while the other is a "nine to five" office building. Water treatment requirements in these two buildings may be quite different.
- Two steam generating systems in an industrial plant may appear to be identical, but process contamination may put a little oil into one condensate system. A boiler water treatment program that is effective in the clean boiler may not perform well in the dirty boiler. Process contamination of a boiler or cooling water system may appear suddenly or very slowly, and may not be repairable without a full plant or building shutdown. Chemical programs therefore must be adjusted to manage the contamination.

It is easy to think of many other situations that could make water treatment problems in one facility different from others.

The tool for obtaining this detailed information about operating facilities is called a plant survey. A survey is essential when taking over a new account, whether it is new construction or an existing, operating system. Existing accounts should be resurveyed whenever new construction is added or significant changes in operating practices are required.

Invest the time to do this survey job thoroughly. The collected information will help to identify critical systems and avoid fatal errors that may have been made in the past.

9.2 RANGE OF SYSTEMS

It is important to understand the range of systems that fall under the general classifications of boilers, open and closed cooling systems, pretreatment trains, etc.

- Boiler water systems range from simple steam heating boilers to 1000 psig industrial boilers and supercritical power generating systems. The general principles of steam generation are the same for all these systems, but the details of operation and the water treatment requirements are vastly different.
- Similarly, open and closed cooling water systems range from simple HVAC chiller systems to high-pressure power stations and critical data processing centers that cannot be shut down.
- Water preparation (pretreatment) trains include both simple filtration of cooling water makeup to remove river mud, and complex demineralization

and sterilization plants that prepare ultrapure water for pharmaceutical and computer chip manufacturing plants.

Many manufacturing plants and commercial facilities contain both HVAC systems and process systems that have different performance requirements. These systems must be completely understood and, if necessary, treated and controlled separately.

It is therefore very important, when starting water treatment in a new facility or taking over treatment of an existing facility, to invest the time to do a thorough survey of each system. The survey information will help to identify critical components that must be treated properly and avoid past errors in older systems.

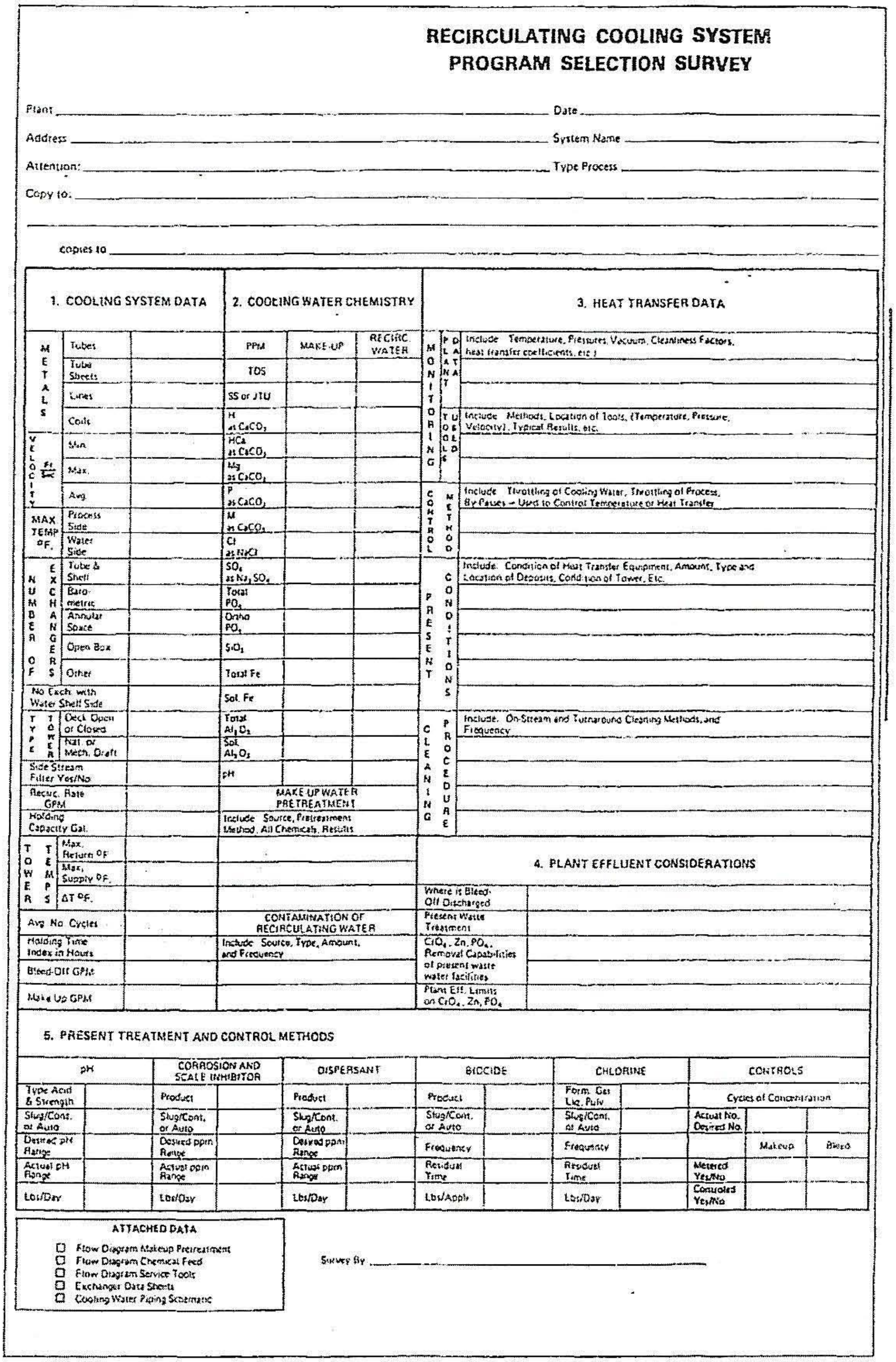
9.3 SOURCES OF INFORMATION

The information in this section is general but comprehensive. It is not likely to apply completely to any specific facility. The principles, however, involving a thorough investigation of the plant equipment, operations, water treatment experience and past history, apply in every case. A simple commercial HVAC system should not require all of the work described in this section, but a complex petrochemical plant may require all of this and more.

When performing a plant survey, choose applicable information from this section, and use it together with detailed boiler and cooling water survey information from chapters 3 and 4. This detailed investigation of a facility is the same approach that a consultant would use in investigating a plant failure.

9.3.1 Systems and equipment

- As-built drawings. Ask to see these, and ask a knowledgeable engineer to go over them with you. Do the as-built drawings differ from the original plans? If so, how? Sometimes changes made during construction, usually to increase capacity or save money, can affect the ability of a water system to function properly. Identify all critical components on the drawings and note design operating temperatures, pressures and flows.
- Walk the systems with a knowledgeable guide, and compare design data with actual pressures, temperatures and flows. This is particularly important for heat exchangers in which water flow is throttled to control a process side outlet temperature. Table 1-12 is an example of a cooling water survey form that can be used to record plant data as it is collected. Collect as much of this information as possible. Make a similar Table appropriate for each plant and water system that is surveyed. Also, make a flow diagram of the system and check it with plant personnel. Identify critical components and mark temperatures, flows, etc. on this drawing.



RECIRCULATING COOLING SYSTEM PROGRAM SELECTION SURVEY

Plant ____________________ Date ____________
Address ____________________ System Name ____________
Attention: ____________________ Type Process ____________
Copy to: ____________________

copies to ____________________

1. COOLING SYSTEM DATA

METALS	Tubes	
	Tube Sheets	
	Lines	
	Coils	
VELOCITY Ft/Sec	Min.	
	Max.	
	Avg.	
MAX TEMP °F.	Process Side	
	Water Side	
NUMBER OF EXCHANGERS	Tube & Shell	
	Barometric	
	Annular Space	
	Open Box	
	Other	
No Exch. with Water Shell Side		
TYPE TOWER	Deck Open or Closed	
	Nat. or Mech. Draft	
Side Stream Filter Yes/No		
Recirc. Rate GPM		
Holding Capacity Gal.		
TOWER TEMPS	Max. Return °F	
	Max. Supply °F.	
	ΔT °F.	
Avg. No. Cycles		
Holding Time Index in Hours		
Bleed-Off GPM		
Make Up GPM		

2. COOLING WATER CHEMISTRY

PPM	MAKE-UP	RECIRC. WATER
TDS		
SS or JTU		
H as $CaCO_3$		
HCa as $CaCO_3$		
Mg as $CaCO_3$		
P as $CaCO_3$		
M as $CaCO_3$		
Cl as NaCl		
SO_4 as Na_2SO_4		
Total PO_4		
Ortho PO_4		
SiO_2		
Total Fe		
Sol. Fe		
Total Al_2O_3		
Sol. Al_2O_3		
pH		

MAKE UP WATER PRETREATMENT

Include Source, Pretreatment Method, All Chemicals, Results

CONTAMINATION OF RECIRCULATING WATER

Include Source, Type, Amount, and Frequency

3. HEAT TRANSFER DATA

MONITORING	PLANT DATA	Include Temperature, Pressures, Vacuum, Cleanliness Factors, heat transfer coefficients, etc.)
	TOOLS USED	Include Methods, Location of Tools, (Temperature, Pressure, Velocity), Typical Results, etc.
CONTROL	METHOD	Include Throttling of Cooling Water, Throttling of Process, By Passes – Used to Control Temperature or Heat Transfer
PRESENT	CONDITIONS	Include: Condition of Heat Transfer Equipment, Amount, Type and Location of Deposits, Condition of Tower, Etc.
CLEANING	PROCEDURE	Include: On-Stream and Turnaround Cleaning Methods, and Frequency

4. PLANT EFFLUENT CONSIDERATIONS

Where is Bleed-Off Discharged	
Present Waste Treatment	
CrO_4, Zn, PO_4, Removal Capabilities of present waste water facilities	
Plant Eff. Limits on CrO_4, Zn, PO_4	

5. PRESENT TREATMENT AND CONTROL METHODS

pH		CORROSION AND SCALE INHIBITOR		DISPERSANT		BIOCIDE		CHLORINE		CONTROLS		
Type Acid & Strength		Product		Product		Product		Form. Gas Liq. Pulv.		Cycles of Concentration		
Slug/Cont. or Auto		Slug/Cont. or Auto		Slug/Cont. or Auto		Slug/Cont. or Auto		Slug/Cont. or Auto		Actual No. Desired No.		
Desired pH Range		Desired ppm Range		Desired ppm Range		Frequency		Frequency			Makeup	Bleed
Actual pH Range		Actual ppm Range		Actual ppm Range		Residual Time		Residual Time		Metered Yes/No		
Lbs/Day		Lbs/Day		Lbs/Day		Lbs/Appl.		Lbs/Day		Controled Yes/No		

ATTACHED DATA

- ☐ Flow Diagram Makeup Pretreatment
- ☐ Flow Diagram Chemical Feed
- ☐ Flow Diagram Service Tools
- ☐ Exchanger Data Sheets
- ☐ Cooling Water Piping Schematic

Survey By ____________________

Table 1-12. Typical recirculating cooling system survey form.

- Water system specifications. As above, compare actual operations with design. If the circulation rate and overall temperature rise differ significantly from design, find out why. For example, heat exchangers may be operating above design capacity, creating a more corrosive and more severely scaling environment. Enter the data on the survey form (Table 1-12).
- Estimate system volumes. If the data are not available, volumes can be estimated from pipe and basin capacities on the drawings. In open cooling systems, a simple salt addition test can be used to measure the volume (see chapter 4).

9.3.2 Operating Data

- Operating procedures. It is very important to understand exactly how the facility operates. For example: Are boilers base loaded or are they "swing" or "peaking" boilers? Does a commercial building operate "9 to 5" or "24-7"? Does the system include "free cooling" (see chapter 4)? Does the building contain critical cooling systems, i.e. a data center cooling system that cannot be shut down? Do any systems have specific and unusual requirements, i.e. mold cooling in a steel mill?
- Water treatment logs. Enter current or proposed water chemistry control limits, e.g. pH and conductivity, and the appropriate chemical control levels for each boiler and cooling system in an appropriate version of Table 1-12 (see chapters 3 and 4). Note the type of feeding, control and data collection equipment in use (or planned, for a new facility). Study the facility log sheets to determine how well the operators maintain their control parameters. This study often becomes a source of future upgrade recommendations. Note frequency and type of testing, and the neatness and quality of the logs. This can be an indication of the commitment that the operating staff makes to water treatment work.
- Current vendor service reports. How frequently and how well is the facility serviced? Are there opportunities for improvement? Do vendor and engineer test data agree? How well does the facility staff respond to requests for changes, repairs and upgrades?
- Current performance data. Inspect corrosion coupon racks and coupons, and take samples of waters and deposits for complete laboratory analyses. The data will help in defining existing problems and needed solutions. See section 10, below on interpretation of analyses. Inspect open equipment and take photographs wherever possible. Inspection photographs make a valuable record for use in evaluating future progress.

9.3.3 Historical Data

- Previous water treatment logs and service reports. Study these records carefully. Identify previous water treatment programs and problems, and discuss these with facility engineers. Remember the truism that "those who do not know history are destined to repeat it."
- Maintenance and inspection records. In a large facility that has separate maintenance and engineering staffs, the maintenance and inspection records can be a valuable source of information on water system performance. Failures will be thoroughly documented, and photographic inspection records will clearly show the condition of operating equipment over time.

9.3.4 Personnel

Facility personnel can be a valuable source of information about operations, and about the past and present status of the water systems. Ask about problems and about changes the staff thinks should be made. A note of caution, however: do not accept information offered by any one individual at face value. Memories are faulty, and opinions about system conditions often vary. Talk to as many people as possible, and check information against inspection and operating records.

There are important aspects of water treatment operations that may not be recorded, but are very important. One example of this problem is the cleaning of new water systems before they are put into service. All new piping should be cleaned to remove oil, mill scale and debris (see chapter 4 in this manual). Even though this work is usually included in the original water treatment specification, the work is rarely documented, and it is not always done. Facility engineers should have this information. If the facility was not started up properly, there will often be an increased tendency for corrosion and deposit problems in system piping. This should be considered when planning the water treatment program.

Identify the water system issues that concern management and the operations staff. These two groups may have different views. For example: operations may be worried about metal failures that limit their on-line time, while management may be concerned about operating costs.

9.4 PREPARING THE SURVEY AND PROPOSAL

- There are two cardinal rules that should be followed in preparing a facility survey and a new proposal for water treatment:
  1. Never assume that anything the facility is doing, or has done in the past, is the best or only way, even though the facility may have requested duplication of an existing program. Start from scratch and

design the treatment program and operating conditions using the best available technology.

2. Remember that internal chemical treatment of boilers and cooling systems should always be the last step, after plant operations and pretreatment systems (chapter 2) have been optimized. Substituting internal chemical treatment for equipment repairs or upgrades plus effective pretreatment and control of operating conditions, invariably leads to costly chemical programs and less than optimum results.

- Use the collected survey information as the technical basis for the proposal. Try to avoid recommending a program that is used elsewhere in the area just because it is successful, or because the customer requested it. Make sure it is right for this facility.
- Design the new chemical treatment program around the most critical components in the system. A less effective or less costly program might protect 99 percent of the system successfully, but if one critical component corrodes, or loses heat transfer capability due to mineral scale formation, the entire program fails.
- Plan locations for chemical additions, corrosion coupon racks, monitoring equipment, etc. carefully. Follow the recommendations in chapters 3 and 4 in this manual. Never assume, without checking, that existing chemical feed locations are correct. Check the locations and determine that pressure drops are sufficient. As an example, many boilers have failed because chemicals were fed incorrectly and therefore could not do their jobs properly (see chapters 2 and 3).

10.0 Interpreting Water Analyses

10.1 INTRODUCTION

Although uses of analytical data are of course specific to pretreatment, boiler water and cooling water applications, the general principles for interpreting analytical data apply to all systems, and are therefore included in this chapter on general water treatment knowledge.

The single most important tool available to water treatment professionals in studying systems, planning chemical treatment programs, controlling operations, evaluating results and investigating problems, is analytical data. Service reports, facility water treatment logs, laboratory water and deposit analyses, microbiological tests, corrosion coupon tests, etc. are the record of past and present system performance and the basis for future planning. Analytical data contain explanations for past failures, and a responsive study of current data can help to prevent future problems.

Analytical work serves no purpose except to consume time and money, unless the data are put to work. Do not let valuable data gather dust in logbooks and service files. Use the data to monitor system performance and train water treatment and facility personnel. Analytical data and performance results should also serve as documentation for new recommendations.

An obvious corollary of all this, but a point that needs to be emphasized, is: never report that system conditions are better than they really are, as shown by the data. Questionable results and negative trends do not go away just because they are ignored. Small problems can be fixed easily, usually with minimum effort and cost. If not resolved, however, these same problems can lead to major system cleanings and equipment repairs. Read water treatment data regularly, face problems squarely and work with facility personnel to make necessary changes and improvements.

10.2 GUIDELINES FOR INTERPRETING WATER ANALYSES

Following are a set of guidelines for use in interpreting water analyses. These guidelines are based on water chemistry discussed in this section, and on water treatment information in chapters 2, 3 and 4. The guidelines are general in nature and must be interpreted in terms of the specific analysis and specific water system under study.

10.2.1 Suitability

Review the analysis for suitability. Does the analysis as a whole match the system? Are there single parameters that just don't seem to be right? This, of course, is a matter of experience. If one or more parameters appear to be completely unrealistic for the system, have them retested if possible before proceeding with final interpretation of the overall water analysis. Interpretations based on wrong data can lead to serious problems.

10.2.2 Accuracy and Completeness

Laboratory water analyses are usually complete and accurate. Errors do creep in, however. For that reason, the first step in interpreting an analysis should be to check the accuracy and completeness of the data. Since electrical neutrality must be preserved (section 8.2.3), the analysis can be tested by comparing the equivalents of anions and cations in the analysis, as shown in section 3.4.3.

The common denominator most often used for these calculations is calcium carbonate, simply because calcium and alkalinity are often already expressed as calcium carbonate and the equivalent weight of calcium carbonate, 50, makes the conversions easy. Table 1-13 shows calcium carbonate conversion factors for some ions commonly listed in water analyses:

TABLE 1-13
Calcium Carbonate Conversion Factors

Ion	As	Conversion factor to calcium carbonate
Calcium	Ca^{+2}	2.50
Iron	Fe^{+3}	2.69
Magnesium	Mg^{+2}	4.10
Potassium	K^{+}	1.28
Sodium	Na^{+}	2.18
Zinc	Zn^{+2}	1.53
Chloride	Cl^{-}	1.41
Nitrate	NO_3^{-}	0.81
Phosphate	PO_4^{-3}	1.58
Sulfate	SO_4^{-2}	1.04

Calculation of the ion balance for all the ions in a complete water analysis is time consuming. However, a simple spreadsheet program can be written to do this work and calculate the cation/anion ratio for the analysis. The ratio should be 1.0. Ratios between 0.9 and 1.1 are acceptable. Ratios outside this range usually mean that something has been missed in the analysis, or that one or more parameters should be retested.

10.2.3 Suspended Solids

Boiler feed water should be clear, and cooling tower makeup water should have very low suspended solids, preferably below 1 mg/L. There is no point in adding suspended matter to a cooling tower unless the chemical treatment program is specifically designed to manage these solids. Circulating cooling water suspended solids should ideally be below 5 mg/L. Higher levels of suspended solids should be filtered and analyzed to determine the source. Most suspended solids are combinations of iron oxide corrosion products, water and wind-blown dirt and microbiological matter.

10.2.4 pH, Alkalinity and LSI

Alkalinity and pH should be in compatible ranges (section 6.4.5). High alkalinity with lower than normal pH, or the reverse, may indicate an analytical error or the presence of noncarbonate alkalinity. If the pH and alkalinity are within range, calculate the LSI of the water (section 7.3). The LSI provides an indication of the scaling tendency of the water.

10.2.5 Conductivity and Cycles of Concentration

Cycles of concentration, as defined in chapter 4, is the ratio of the concentration of an ion in the circulating tower water divided by the concentration of the same ion in the makeup water. Calculate cycles for conductivity, alkalinity (unless acid is fed to the system), calcium, magnesium, potassium, sodium, chloride, silica and sulfate. Cycles should also be calculated for phosphate if it is present in the makeup water and not included in the treatment program. In specific systems, cycles can be calculated for other ions, such as nitrate, that may be present in the makeup water. Compare these calculations with cycles calculated from water use: makeup flow divided by blowdown plus evaporation. See chapter 4 for details.

In a well-run cooling system with no problems, the conductivity will be close to but below the upper limit established for the chemical treatment program (chapter 4). Cycles will be the same for all ions, within about 10-15 percent. If significant calcium carbonate scale is precipitating, cycles based on calcium and alkalinity will be low compared to other data. If phosphate is present in the makeup water and calcium and phosphate cycles are low, calcium phosphate scale may be forming. Note: phosphate added as a treatment chemical will mask phosphate cycles. Similar cycle calculations can show possible formation of silica and calcium sulfate scales.

10.2.6 Corrosion Control

A complete water analysis will include iron, copper and zinc, plus the inorganic chemicals added as corrosion inhibitors. Interpretation of these data requires knowledge of the system. Makeup levels of iron, copper and zinc should be very low or zero. If these ions are present in the makeup water, they should concentrate (cycle) with the water. Low cycles represent precipitation and possible deposit formation.

High cycles of these elements may indicate corrosion. However, many cooling and boiler systems contain iron oxide deposits that can be a source of suspended or colloidal iron oxides in the water. If iron levels are greater than 1 mg/L, soluble (filtered) and total iron should be run. Suspended iron oxide is determined by difference. These data will provide guidance for designing or changing the chemical treatment program.

Zinc in a cooling water analysis, if not present in the chemical treatment program, is generally a sign of corrosion of galvanized components. Copper is also a sign of corrosion. Copper levels should never by higher than 0.3 mg/L in circulating cooling water. Even low levels of copper, together with zinc, can be a serious warning of galvanic corrosion of zinc (section 8.4.1). Corrosion problems in boiler and cooling water systems are covered in chapters 3 and 4.

10.3 AN EXAMPLE OF INTERPRETATION OF ANALYTICAL DATA

This section is an explanation of a typical cooling water analysis, to illustrate what can be learned from a detailed study of analytical data as described in section 10.2. The discussion requires knowledge of cooling water chemistry that is explained in chapter 4. New readers may wish to scan this section, and then return to it for study after reading chapter 4.

Table 1-14 is a typical laboratory analytical report, showing raw well water, softened makeup water, circulating cooling tower water, and a closed cooling system water. These data are used as examples to illustrate what can be learned from routine analyses of boiler and cooling water samples. Refer to section 10.2 while reading this section.

TABLE 1-14

Cooling System Water Analyses

		Water sources, data in mg/L except *				
Parameter	**As**	**City**	**Softened**	**Tower**	**Cycles**	**Chilled**
pH*	pH	7.16	7.18	8.83		9.7
Conductivity*	umhos	391	472	1700	3.6	6080
Total alkalinity	$CaCO_3$	99.9	133	512	3.8	1910
Total suspended solids	mg/L	<0.1	0.1	2.9		79
Aluminum	Al	<0.1	<0.1	<0.1		<0.1
Boron	B	0.02	0.02	0.11		118
Calcium	$CaCO_3$	95.5	5.58	52.8	9.5	13.0
Chromium	Cr	<0.01	0.03	<0.01		6.60
Copper	Cu	<0.01	0.02	0.05		0.40
Iron - soluble	Fe	0.13	0.26	0.18		0.21
Iron - total	Fe	0.14	0.26	2.67		39.7
Lead	Pb	<0.01	<0.01	<0.01		0.20
Magnesium	$CaCO_3$	26.7	4.26	35.7	8.4	21.5
Manganese	Mn	<0.01	<0.01	0.01		0.20
Molybdenum	Mo	0.02	<0.01	15.0		0.10
Potassium	K	2.17	0.83	3.93	4.7	5.90
Sodium	Na	31.1	104	427	4.1	1285
Strontium	Sr	0.13	<0.01	0.05		0.02
Zinc - soluble	Zn	<0.01	0.01	2.51		
Zinc - total	Zn	<0.01	0.02	3.39		1.84
Bromide	Br	<1.0	<1.0	1.32		<2.0
Chloride	Cl	49.6	61.1	246	4.0	60.3
Fluoride	F	0.50	0.99	3.21		<1.0
Nitrate	NO_3	8.95	9.65	39.2	4.1	35.0
Nitrite	NO_2	<0.25	<0.25	<0.25		252
Orthophosphate	PO_4	<0.2	<0.2	0.15		<0.2
Polyphosphate	PO_4	<0.2	<0.2	13.9		
Total phosphate	PO_4	<0.2	<0.2	19.8		<0.2
Silica	SiO_2	10.9	11.1	49.4	4.5	12.1
Sulfate	SO_4	18.2	20.0	90.0	4.5	21.7
Cation/anion ratio		0.92	0.99	0.94		1.02
LSI @ 100 F		-0.46	-1.58	1.61		2.2

Table 1-14. Cooling system water analyses.

10.3.1 First Observations

- The ratios for the four water analyses in Table 1-14 are all between 0.9 and 1.1, an acceptable range indicating that the analytical data are correct and that no important ions have been missed.
- Conductivity in the tower water is high, but is supported by the high alkalinity and pH.
- Hardness in the softened water indicates possible poor operation of the softening equipment.
- Very high conductivity, suspended solids and iron in the chilled water indicate problems to be explained in this system.

10.3.2 Corrosion Control

Table 1-14 shows that the city water does not contain significant amounts of phosphate, zinc and molybdate. The tower water contains 15 mg/L molybdenum, 13.9 mg/L polyphosphate, and 3.4 mg/L total zinc. These are the active corrosion inhibitors in the treatment program. The levels can be compared with the recommended levels, as discussed in chapter 4.

The copper level in the tower water is very low, indicating good corrosion protection on copper. The total iron level, however, is high at 2.87 mg/L. The iron value can not be interpreted without further information. At the high pH in the tower water, most of the iron should be insoluble, appearing as total iron in the analysis. If coupon corrosion rates are low, and if the system has a history of iron deposits, then the iron shown in the analysis is probably dispersed from elsewhere in the system by the action of the chemical program. Alternatively, if corrosion rates are high, the iron may be newly formed corrosion product.

When zinc is used as a corrosion inhibitor in cooling water (chapter 4), especially in high pH systems, a portion of the zinc precipitates as colloidal zinc hydroxide. The chemical program should be designed to maintain 50 percent or more of the zinc soluble, to provide corrosion protection. In this case, about 75 percent of the zinc is soluble. This is one indication that corrosion rates on steel are probably low and the iron in the water is dispersed from deposits.

10.3.3 Mineral Scale Control

The pH of the tower water is 8.83, indicating that no acid is fed to this system for pH control. The +1.61 value for the Langelier Stability Index (LSI) places this water in calcium carbonate scaling territory (section 7.3). The chemical program should therefore contain specific carbonate scale control chemicals. With polyphosphate added for corrosion protection, there is also a possibility for calcium phosphate scale formation.

The difference between the total phosphate and polyphosphate values in the tower water (Table 1-14) shows that there is roughly 6 mg/L of organic phosphate in the water, added for calcium carbonate scale control (chapter 4). Organic polymeric scale control chemicals may also be present, but these will not appear in the analysis.

The cooling tower makeup in this case is the softened water. Table 1-14 shows that with the exception of calcium and magnesium, cycles average about 4.0, indicating that the system is well controlled. The fact that sulfate is at 4.5 cycles is further proof that no sulfuric acid is fed to the tower water.

However, cycles based on calcium and magnesium are close to double the average in this system. This is an unusual problem. If calcium carbonate were precipitating, the cycles based on calcium and alkalinity should be below the average for other parameters. The high calcium and magnesium hardness values, on the other hand, show a problem with softener operation. Hardness is periodically "breaking through" the softener, as explained in chapter 2. Hardness levels in the softened water (Table 1-14) are too high, and the tower water data indicate that the values must occasionally be even higher than this. The softener should be inspected and the operation corrected. However, it is not a good idea to use zero soft water as cooling tower makeup. See chapter 4 for more on this subject.

The high hardness levels may obscure any loss in cycles due to precipitation of calcium carbonate and/or calcium phosphate. At least, the fact that alkalinity is at 4 cycles is evidence that calcium carbonate is not precipitating. Nothing can be said about calcium phosphate scale formation from this analysis alone.

10.3.4 Chilled Water Analysis

The chilled water analysis in Table 1-14 presents a different set of problems. This water is in poor condition. The very high conductivity and sodium levels indicate that this is probably "old" water that has been in the system for some time. Chemicals have been added periodically, probably to maintain treatment levels, and the resulting increase in dissolved solids (conductivity) has increased the corrosivity of the water (section 8.3.2).

The suspended solids level, at 79 mg/L, is very high. Most of these solids are probably iron oxides, as shown by the 39.7 mg/L of iron in the system. At pH 9.7, almost none of this iron will be soluble. The iron may be a mixture of new corrosion products and old deposits dispersed in the water. Evidence of old deposits comes from the 6.6 mg/L of chromium in the water. Chromium comes from deposits formed in days when chromate was used as a corrosion inhibitor.

Further evidence of corrosion in this system comes from the presence of 1.84 mg/L zinc in the water. The most likely source of the zinc is corrosion of galvanized steel, and this is supported by the 0.2 mg/L lead. Small amounts of lead are found in hot-dipped galvanized steel coatings. Galvanized steel is not a suitable material for use in water at pH above 9 (see chapter 4), and this problem is aggravated by the copper in the water. Even small amounts of copper can aggravate corrosion of zinc by precipitating as copper metal to form galvanic cells on the galvanized surface (section 8.4.1 and chapter 4).

Finally, boron (as borate) and nitrite are components of the chemical treatment program in the chilled water. The borate level is high, indicating repeated additions of product to the system, and nitrite is very low. Borate is a pH buffer, and nitrite is the corrosion inhibitor for steel. The level of nitrite is too low to maintain protection. The nitrate in the water comes from oxidation of nitrite, possibly from air inleakage of dissolved oxygen in makeup water. Evidence of microbiological activity comes from the fact that the combined nitrite + nitrate level is too low to match the borate (chapter 4). Nitrite has been lost, possibly by microbiological reduction to nitrogen gas.

Responses to these chilled water problems are site-specific, but must be designed to clean the system, control oxygen and microbiological problems, and establish good corrosion control. Chilled water chemical treatment is discussed in chapter 4.

10.4 USING ANALYTICAL DATA

Operating data from boiler and cooling water systems, and from water preparation trains, are an invaluable resource for any water treatment professional. The explanations for poor results are almost always buried in the control data. Data should be used to document good performance and to identify problems long before they become serious, so that corrective actions can be taken.

Every water treatment document should have a purpose. If it has no purpose, or is not used for that purpose, then it is an expensive waste of valuable time and should be eliminated. By the same token, documents and data that are produced regularly should be used to generate ongoing reports that show system status and needs for action.

This section discusses the information that is available in various water treatment documents, and ways in which these data can be used to monitor and control system performance.

10.4.1 Sources of Information

- Log Sheets. Boiler and cooling system operating personnel should test their water systems regularly. Even with the highly sophisticated, automated feeding and control systems that are explained in chapters 3 and 4, routine testing is important. Systems can and do fail, and control, once lost, may be difficult to regain. Tests to be run are site-specific, but should always include conductivity, pH and at least one test for an active component of the chemical treatment program. Daily testing is best, but tests should always be run at least three times per week.

Testing is even more important in systems that are controlled by pumps and timers or by water meter pulses (see chapter 4). Operators should be trained to use their data to adjust pumps and timers as needed to keep control data within range, and to record their data on trend graphs that provide a visible, ongoing performance record (see section 10.5, below).

Even in so-called "full service" facilities, where the water treatment professional does all the testing and control work, simple daily readings are valuable. Much can go wrong between monthly water treatment vendor visits. Operators can be trained to test pH and conductivity, or to read on-line meters, and to call if the data fall outside the control ranges.

- Service Reports. Water treatment service reports should include all operator tests plus additional tests that include the active components of the treatment program and performance data such as iron and copper. Specific tests to be run and frequency of testing are obviously site-specific. The general rule is that all active components of the treatment program and all significant water chemistry parameters should be tested on a predetermined regular basis and plotted on trend graphs.

  The statement that testing is unnecessary because the results are always the same is not valid. It is important to recognize the universal validity of Murphy's Law. The week that testing is not done is always the week in which the boiler bleed valve will stick and boiler water will carry over to a turbine, or a pH control unit will fail, creating a low or high pH excursion.

- Quarterly Laboratory Analyses. Quarterly analyses are discussed in sections 10.2 and 10.3. Testing should cover all water systems in the facility, and should include water, deposits and microbiological tests as needed (chapter 4).

These tests back up and extend facility and vendor tests, and provide an ongoing detailed overview of system conditions. Other data, e.g. corrosion coupon reports (chapter 4), should be correlated with the analytical results to demonstrate system performance. Quarterly or annual reports based on all of the testing done at the facility should then serve as the basis for meetings at which performance is reviewed and plans for changes or improvements are made and approved.

10.4.2 Trend Graphs

Trend graphs are simply plots of one or more analytical variables vs. time. The graphs should include control ranges, so that out-of-bounds data can easily be recognized. Data trends and correlations among different variables, that might not be recognized in columns of Figures, can easily be seen in trend graphs.

Sophisticated computer programs are available that will automatically plot trend graphs and calculate statistical process control (SPC) charts. SPC charts show numbers of data points, percentages in and out of range, standard deviations from calculated averages, and other statistical parameters.

The fact is, however, that SPC charts and the calculated statistics are rarely used for more than demonstration purposes. The trend graphs themselves visually tell the story and provide all the necessary information.

For that reason, simple spreadsheet programs that automatically plot graphs based on regular data entries are sufficient, and often better than complex SPC programs. The graphs are better quality and more flexible, and the programs are simple enough to be used easily by untrained personnel. Spreadsheet programs can be provided at almost no cost to any facility that has an available computer, and they serve as an inducement to operators to do the testing and enter their own data.

One valuable use of trend graphs is to correlate data and show response to changes in operations. Figure 1-14 shows an example of this application. This manufacturing plant runs an open recirculating cooling water system, using a molybdate-based corrosion control program. During 1991, the dosage of the corrosion control program was controlled by manually adjusting the chemical pump, and conductivity (blowdown) was controlled by a conductivity probe and solenoid valve. In 1992, the chemical feed was changed to water meter control, and the control ranges for molybdate and conductivity were narrowed.

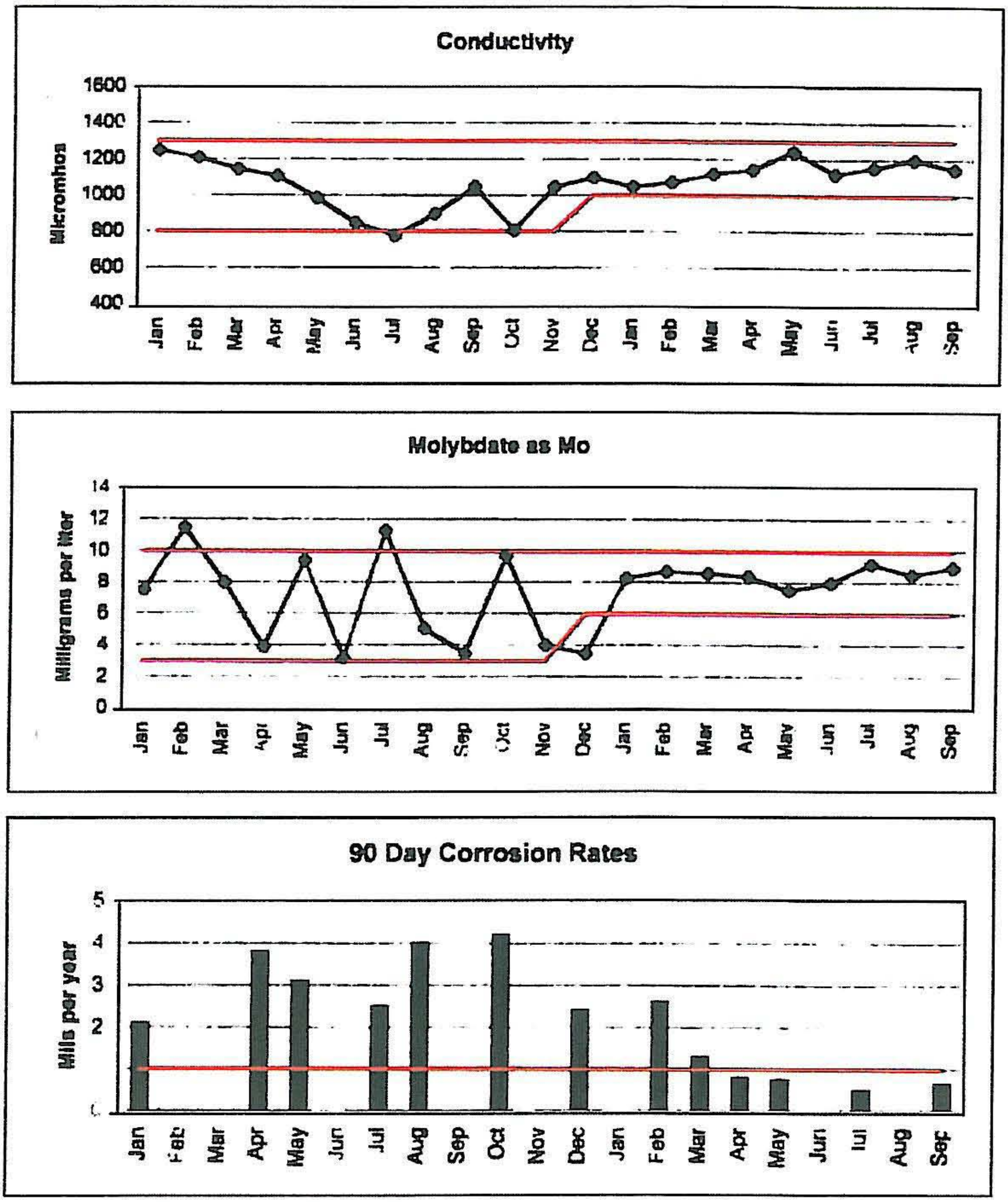


Figure 1-14. Typical trend graph data correlations.

The three spreadsheet trend graphs in Figure 1-14 clearly show the results of the changes in chemical feed method and the narrowed control ranges, and the response of the system in terms of reduced coupon corrosion rates. Visual data analyses such as this make the need for changes in operating procedures clear, and then document the results of these changes.

11.0 Technical References

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CHAPTER 1
TRAINING QUESTIONS

1. The data processing floors in a large commercial bank building require year-round cooling for heat removal. Some portions of one floor are to be left vacant and unheated during a winter season. However, the cooling system that services this floor cannot be isolated and must be allowed to circulate through the unheated area. To prevent freezing of the cooling coils, the chief engineer suggests adding ethylene glycol (antifreeze) to the cooling water, but the building architects very strongly recommend against doing this. Why? What would the effect be on building operations if this change were made? Can you think of any other ways to prevent the unheated cooling coils from freezing? (Section 2.2.2 and Table 1-2).
2. One of the objectives of water treatment is to keep heat transfer surfaces clean. Explain why the cost of operating a building chiller machine, or a steaming boiler, increases as deposits form in the tubes. Sections 1.0, 2.2.3 and 2.3.2).
3. Using the concepts in sections 3.1, 3.2 and 3.3, write chemical formulas for the following compounds commonly encountered in water treatment:

   Sodium sulfite (sulfur valence +4) Calcium hydroxide
   Disodium hydrogen phosphate Hydrogen sulfide

4. Calculate the valence of bromine and nitrogen in the following compounds. In each case, is bromine or nitrogen a cation or an anion? Sections 3.2 and 3.3.

   Sodium bromide, NaBr
   Bromine chloride, BrCl
   Hypobromous acid, HOBr
   Sodium bromate $NaBrO_3$
   Ammonium chloride, NH_4Cl
   Nitrogen gas. N_2
   Sodium nitrite, $NaNO_2$
   Nitric acid, HNO_3

5. Using your own words, define the following analytical chemistry terms:
   - Molecular weight and equivalent or combining weight.
   - Molarity and normality.

   Why are these concepts important in water treatment? (Section 3.4).
6. Following is a typical analysis of a cooling tower water:

Parameter	As	mg/L	CaCO3 conversion factor
Tot. alkalinity	$CaCO_3$	125	1.0
Calcium	Ca	50	2.5
Magnesium	Mg	15	4.1
Sodium	Na	45	2.2
Chloride	Cl	52	1.4
Sulfate	SO_4	125	1.0
Silica	SiO_2	45	1.7

Using the common denominator concept in section 3.4.3, check this analysis for analytical errors, by calculating the cation/anion ratio. Use the calcium carbonate conversion factors shown above. Why is this calculation necessary? Why not just add the cations and anions to see if they match? Use the concepts of equivalent weight, electrical neutrality and common denominators in your answer. As an extra challenge, use the data in Table 3.1 to calculate the calcium carbonate conversion factors shown above. (Section 3.4).

7. The pH of a 10^{-3} N solution of hydrochloric acid is 3, but the pH of a 10^{-3} N solution of citric acid is over 5. Why the difference? (Sections 4.2 and 4.3.1).
8. The ionization constant of pure water at 100°C is 10^{-12}. Calculate the pH of pure water at 100°C. Explain why the pH of pure water is not always 7. (Section 4.3.3).
9. If 1 ml of a sodium hydroxide solution is required to raise the pH of a water sample from 7 to 8, how many ml will be required to raise the same sample from pH 8 to 9? How many from pH 9 to 10? Explain your answer. (Section 4.3.2 and Figure 1-5).
10. Would you expect the pH of a solution of ammonium chloride (NH_4Cl) to be acidic (less than 7), neutral, or basic (greater than 7)? How about a solution of trisodium phosphate? (Section 4.4 and Table 1-5).
11. Explain what is meant by the term "inverse solubility"? Why is this important in water treatment? List four substances common in boiler and cooling water systems that are inversely soluble in water. (Sections 5.4 and 5.6).
12. Compare the solubilities of oxygen and carbon dioxide in Figures 1-7 and 1-8. Why is carbon dioxide so much more soluble than oxygen in water? Do both of these gases follow Henry's Law of solubility? Section 5.6.
13. Two different circulating cooling waters are found to have the same total (M) alkalinity and calcium hardness, but different P alkalinity values. For each water, calculate the carbonate, bicarbonate and hydroxide values, and the LSI value. What problems would you expect to find in these cooling systems? Should they be treated the same way? Explain why it is important to know more than just pH and hardness when planning a cooling water chemical treatment program. For both waters, assume a temperature of 100°F and a conductivity of 500 microsiemens/cm. (Sections 6.0 and 7.0).

Water A:		Water B:	
	pH = 8.4		pH = 8.9
	Ca as $CaCO_3$ = 250		Ca as $CaCO_3$ = 250
	M = 250		M = 250
	P = 10		P = 130

14. Is the LSI a good indicator of the corrosivity of a circulating cooling water? Explain your answer. (Section 7.3).
15. Explain the basic corrosion process on steel in cooling water. (Section 8.0).

16. Why are oxygen scavengers an important part of most boiler water treatment programs? (Section 8.2 and chapter 3, section 7.2).
17. A steel pipe nipple is screwed into a brass valve in a cooling water system. What problems might occur in this system, and why? How could these problems be prevented? (Section 8.4).
18. Explain the difference between polarization and passivation as they relate to the corrosion of steel in water. (Sections 8.3.3 and 8.4.2).
19. Describe the importance of system surveys as the basis for proposals in new accounts. (Sections 9.1 and 9.2).
20. List the four essential sources of information required for a complete facility survey, and explain why each is important. Use examples in your answer where possible. (Section 9.3).
21. Interpret the two sets of water analyses and facility information in the Table on the following page. Calculate LSI values and cycles of concentration, and explain the problems you should expect to find in each system. Use all of chapter 1, especially section 10.3, and the cooling water treatment information in chapter 4.

Water Analyses from Operating Cooling Towers

Facility A

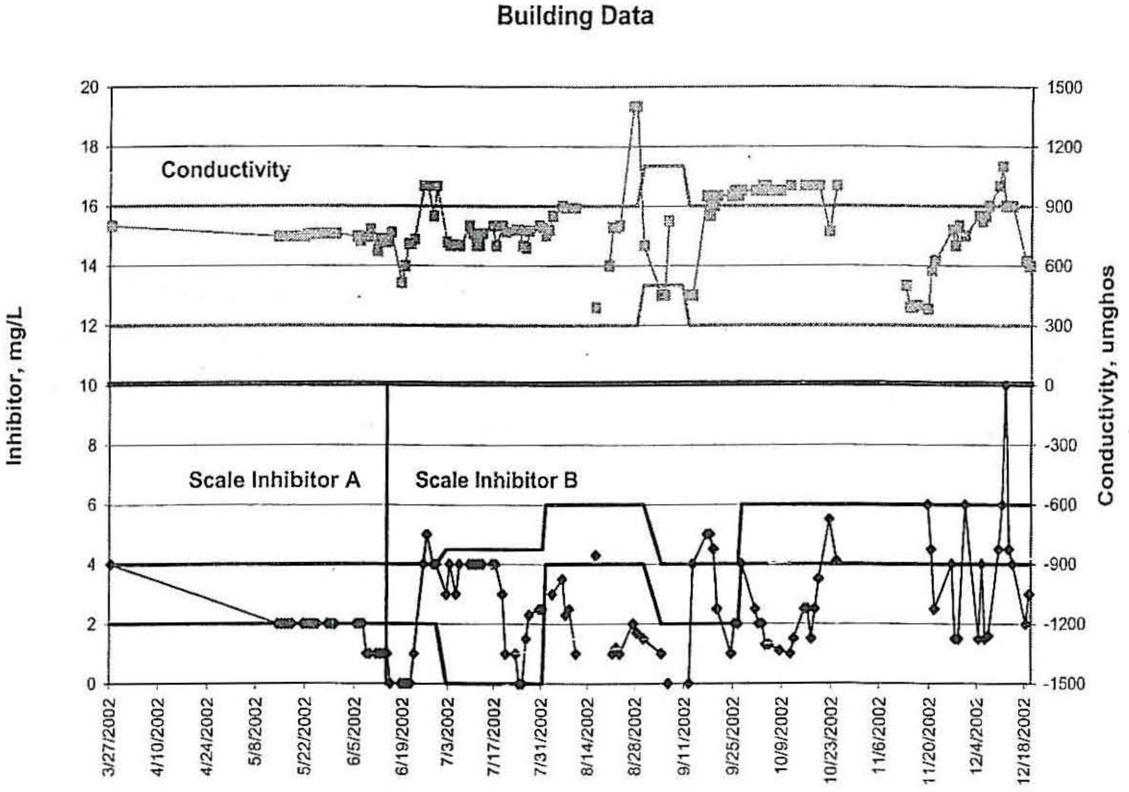
A commercial high-rise office bldg.
Operation 12 hr/day, 5 days/week.
Makeup is city water.

Facility B

A specialty chemical mfg. company
Plant operates continuously.
Makeup is plant well water.

		Facility A			Facility B		
Parameter	As	Makeup	Tower	Cycles	Makeup	Tower	Cycles
pH	pH	6.9	6.5		7.7	8.7	
M alkalinity	$CaCO_3$	18.1	22.4		124	150	
Conductivity	µmhos/cm.	87.1	730		294	504	
Tot. susp. Solids	mg/L	0.5	25.4		0.1	1.65	
Calcium	$CaCO_3$	20.1	164		106	132	
Magnesium	$CaCO_3$	8.21	56.7		30.8	56.2	
Iron – total	Fe	0.20	7.15		0.01	0.07	
Copper	Cu	.014	0.75		0.84	0.30	
Molybdenum	Mo	<0.01	3.27		<0.01	<0.01	
Sodium	Na	7.89	70.6		16.5	33.9	
Zinc – total	Zn	0.05	.021		0.15	6.51	
Zinc – soluble	Zn	0.03	0.75		0.12	0.92	
Bromide	Br	<0.2	74.5		<0.2	0.22	
Chloride	Cl	10.3	101		16.8	34.6	
Sulfate	SO_4	7.50	27.8		7.31	14.7	
Orthophosphate	PO_4	0.29	1.49		0.12	3.58	
Total phosphate	PO_4	0.31	1.54		0.15	4.23	
Silica	SiO_2	3.62	26.7		11.1	21.1	
LSI at 100 °F	LSI						

22. Discuss the following trend graph. What problems do you see and how could they be corrected? Section 10.4.2 and chapter 4.



ANSWERS TO CHAPTER 1 TRAINING QUESTIONS

Answer to Question 1

The specific heat (heat capacity) of an optimum ethylene glycol/water mixture is about two-thirds that of water. If the cooling system were filled with a glycol/water mixture, it would remove only two-thirds as much heat from the building and might not be able to provide sufficient cooling to the data processing center.

The best way to solve this problem is to install the necessary valves and piping so that the cooling system in the unused sections can be isolated and drained. Alternatively, bypass piping can be installed around each fan coil so that the coils can be drained. Sometimes the fan coils are isolated and filled with ethylene glycol solution, but this creates microbiological fouling problems when the system is returned to operation.

Answer to Question 2

Deposits insulate the tube surfaces and restrict heat transfer. Deposits that form in heat transfer tubes act as insulation. This means that less heat is transferred, and the process becomes less efficient. More fuel must be burned to maintain steam production, and chillers must run longer to maintain the chilled water temperature. Eventually, boiler tubes may fail from overheating, and the chiller machine may be unable to produce chilled water at the required temperature.

Answer to Question 3

Sodium sulfite (sulfur valence +4)	Na_2SO_3
Calcium hydroxide	Na_2HPO_4
Disodium hydrogen phosphate	$Ca(OH)_2$
Hydrogen sulfide	H_2S

reverse $NA_2HPO_4 + Ca(OH_2)$

Answer to Question 4

NaBr	Br = -1	Anion
BrCl	Br = +1	Cation
HOBr	Br = +1	Complex anion
$NaBrO_3$	Br = +5	Complex anion
NH_4Cl	N = -3	Complex cation
N_2	N = 0	Neither – nonionized gas.
$NaNO_2$	N = +3	Complex anion
HNO_3	N = +5	Complex anion

Answer to Question 5

- Molecular weight: The sum of the atomic weights of the elements in a compound.
- Equivalent or combining weight: The weight of a compound that will react with an equivalent weight of another compound. This is usually the molecular weight divided by the valence of the reactive element in the compound.
- Mole and molarity: A mole is one molecular weight of a compound expressed in grams. A one molar solution is one mole of a compound dissolved in one liter of water.
- Equivalent and normality: An equivalent is one equivalent weight of a substance expressed in grams. A one normal solution is one equivalent weight of a compound, in grams, dissolved in one liter of water.

These concepts are needed in calculating the results of analytical tests, the amounts of acid, base and other chemicals needed in chemical treatment, etc.

Answer to Question 6

Multiply mg/L x conversion factor to get calcium carbonate equivalents, and add the cations and anions separately (alkalinity is an anion). The cation/anion ratio is 1.04. The analysis is correct.

Equal concentrations of different substances, in mg/L, contain different numbers of ions because they have different molecular weights and the ions have different charges. To compare the analytical data, the data must be converted to an equivalent (common denominator) basis so that electrical neutrality is preserved in the solution.

To convert each analysis to a calcium carbonate equivalent, divide by the equivalent weight of the ion and multiply by the equivalent weight of calcium carbonate.

Answer to Question 7

Hydrochloric acid is a strong acid that is completely ionized in solution. Citric acid is a weak acid that is only partially ionized.

Answer to Question 8

At 100°C, $[H^+][OH^-] = 10^{-12}$. Therefore, $[H^+] = 10^{-6}$ and the pH = 6. Ionization and equilibrium constants increase with increasing temperature. To avoid confusion, pH data are normally reported at 25°C, using temperature-compensating pH probes. Colorimetric pH measurements are not temperature-compensated, so the solution must be cooled to about 25°C before the pH is measured.

Answer to Question 9

Answer: 10 ml from pH 8 to 9, and 100 ml from pH 9 to 10. pH is a logarithmic function. Each unit increase in pH requires tenfold more base.

Answer to Question 10

Ammonium chloride solutions are acidic because ammonium hydroxide is a weak base and hydrochloric acid is a strong acid. Similarly, solutions of trisodium phosphate are basic because phosphoric acid is a weak acid and sodium hydroxide is a strong base.

Answer to Question 11

A substance that is inversely soluble becomes less soluble as the temperature increases. This is important because it causes scale to form preferentially on hot heat transfer surfaces. Also, for this reason it is possible to remove dissolved gases from water by boiling the water. Four inversely soluble substances common in water treatment are: calcium carbonate, calcium phosphate, oxygen and carbon dioxide.

Answer to Question 12

Oxygen does not react with water. Carbon dioxide reacts with water to form carbonic acid, which in turn can be neutralized by bases to form carbonates and bicarbonates. Nevertheless, both gases follow Henry's Law.

Answer to Question 13

Answer:	Water A		Water B	
	Carbonate	= 20	Carbonate	= 240
	Bicarbonate	= 230	Bicarbonate	= 0
	Hydroxide	= 0	Hydroxide	= 10
	LSI	= +1.6	LSI	= +2.1

Even though both water have the same total alkalinity and calcium hardness values, water B will have a much greater tendency to form calcium carbonate scale. This can be seen from the LSI values, but more clearly and dramatically from the difference in carbonate levels in the two waters. Different chemical treatment programs will be required for these two systems.

Answer to Question 14

LSI values should never be used to determine the corrosivity of a circulating cooling water. The LSI calculation was developed for municipal water supplies with no heat transfer. In this calculation, corrosion control is assumed to depend upon formation of a protective calcium carbonate film. This does not apply to cooling water systems.

Answer to Question 15

Corrosion is an electrochemical process. It requires a complete electrical circuit, including both the metal and the water. Iron dissolves at points on the metal surface called anodes, and dissolved oxygen in the water is reduced at other points called cathodes. Electrical neutrality must be preserved, so that only equal numbers of ionic charges can react (not necessarily equal numbers of atoms or equal ppm of iron and oxygen).

Answer to Question 16

Reduction of dissolved oxygen to hydroxide ions is the cathodic corrosion reaction under both cooling and boiler water conditions. Oxygen scavengers remove the last traces of dissolved oxygen from boiler feedwater, thus protecting the boiler tubes and drums from oxygen attack.

Answer to Question 17

This is a case of galvanic corrosion. Steel (iron) is more active in the galvanic series than copper (Table 1-11). Steel becomes the anode and brass the cathode. Steel will corrode more rapidly than it would if not in contact with brass (copper), and the brass will be protected. The threaded steel nipple will corrode rapidly to failure.

It is difficult to prevent galvanic corrosion with chemical treatment. Either use the same metal for both fittings and pipe, or use dielectric (nonconducting) fittings between dissimilar metals, to break the circuit and stop the corrosion current from flowing.

Answer to Question 18

Both processes cover cathodic areas on the surface with films that interfere with the oxygen reduction reaction. Because corrosion rates are controlled by the rate of the cathodic reaction, these processes reduce corrosion rates.

Polarization is a dynamic process. The films are generally layers of hydroxide ions, or in some cases hydrogen gas. These films can be changed or swept away by changing system conditions such as flow velocity, temperature, etc.

Passivation is a similar process, except that the protective films are more permanent in nature. The protective film formed by tolyltriazole on copper, and the aluminum oxide film that forms on aluminum in water, are examples of passive films.

Answer to Question 19

No two commercial buildings or industrial plants are alike, even though they may have been built as sister facilities or may use the same makeup water supply. Design and operating differences may require very different treatment programs in apparently similar facilities. A thorough survey, as described in section 9.0, provides the critical design, operating and cost information needed to prepare proposals that are matched to the facility, technically sound and cost-effective. If possible, provide examples of good and poor system surveys from your own experience.

Answer to Question 20

- Systems and equipment: Provides detailed information about the facility that can affect the design and control of the water treatment program. Examples include metallurgy, water flow rates, critical or throttled heat exchangers, heat loads, operating cycles, etc.
- Operating data: Facility water treatment logs and vendor service reports, equipment inspections, etc. show how well, or poorly, the facility has been operated, and establishes the current condition of pipes, heat exchangers, cooling towers, boilers, etc.
- Historical data: Old water treatment logs, service reports and maintenance records show what problems the facility has faced in the past.
- Personnel interviews: Facility personnel can be a valuable source of information about past and present status of the water systems. Interviews help in identifying the cost and performance issues that are primarily important in the facility, and in identifying critical heat exchangers.

Answer to Question 21

Calculate LSI values and cycles of concentration for each water, and examine the analyses for unusual data that could indicate problems.

Water A:

- LSI values are strongly negative, alkalinity, pH and hardness values are low. This is a soft, corrosive water, even when cycled in the cooling tower.
- The tower is running at 8-9 cycles. Chloride cycles are normal and sulfate cycles are low, showing that no acid is being added to the tower. However, alkalinity does not cycle and the pH is lower than expected at these cycles. This indicates potential microbiological activity in the system (anaerobic organisms generate acids as a result of metabolic processes, chapter 4). Low sulfate cycles indicate possible sulfate-reducing bacteria (SRB) in the system.
- Iron and copper levels are high, indicating ongoing corrosion. Phosphate in the tower water is probably cycled from the makeup. Cycles are low, a possible indication of calcium phosphate precipitation. The only visible chemical treatment in the tower water is a small amount of molybdenum, too low to provide protection in this corrosive water. Since molybdenum is low, tolyltriazole (TT), the logical copper corrosion inhibitor, is probably also low.
- The suspended solids level is very high. The solids should be filtered and analyzed. They are probably a mixture of corrosion products and microbiological matter.
- If zinc is part of the chemical treatment, the levels are too low to provide any protection. Also, zinc is not an effective corrosion inhibitor at this low pH. The zinc may also indicate corrosion of galvanized components in the system.

- This water requires a strong corrosion control program for steel, copper and possibly zinc, plus dispersants for suspended solids and a calcium phosphate scale inhibitor. Sidestream filtration to control suspended solids will be helpful.

Water B:

- The LSI of the tower water is +1.6, well into the calcium carbonate scaling range. The tower is running at about 2 cycles, but calcium and alkalinity are not cycling, indicating calcium carbonate scale formation.
- Copper in the makeup water is very high. This should be retested. If the value is correct, the source of makeup water copper should be found and corrected, to prevent this high level of copper from entering the cooling tower system. Copper is not cycling, indicating precipitation of copper. This creates a danger of galvanic corrosion of steel (chapter 4).
- Galvanized steel should be stable in this water. Therefore, the zinc in the tower water is probably added for corrosion protection of steel. However, the level of soluble zinc is much too low, indicating precipitation at the high pH in this water. If zinc is to be used in this way, strong polymeric stabilizers are needed to prevent this precipitation.
- Orthophosphate is not appropriate in this system and is not added with the chemical program. It is therefore formed in the tower water by chemical or microbiological reversion of polyphosphates or organic phosphonates (chapter 4). Some calcium carbonate scale is probably also precipitating.
- This system requires a strong phosphonate/polymer calcium carbonate scale control program, plus polymers for dispersancy and calcium phosphate control. Microbiological control is also very important in any alkaline system. A bromine release product could be used effectively as an oxidizing biocide, along with a nonoxidizing biocide, but the low bromide level indicates that bromine is not in use in this system.

Answer to Question 22

- Control of the scale inhibitor dosage is very poor. The vendor attempted to improve control by changing the control range, but this was not successful.
- The data show clearly that the scale inhibitor dosage system was not working and should be repaired. Severe mineral scale formation occurred.
- Neither the vendor nor the building personnel in this case responded to the clear evidence of poor dosage control. Trend graphs provide clear early warning of control problems. In this case the warnings were ignored.
- Conductivity (cycles) also show an upward trend, further complicating the scaling problem. Early response to the data could have kept this system in good condition.

2. CHAPTER 2

External Treatment (Pretreatment)

Table of Contents

CHAPTER 2

Pretreatment

1.0 Introduction

1.1 OVERVIEW

Chapter 2 discusses pretreatment, or external water treatment technology. Pretreatment, as used in this context, means mechanical and chemical treatment of a raw makeup water supply, to make the water suitable for use as boiler feedwater, cooling tower makeup, or process water.

As explained in Chapter 1, the two related primary objectives of water treatment are to keep heat transfer systems clean and to protect the system equipment from corrosion and fouling damage. Makeup water supplies vary widely in both quality and purity, and available supplies may not be suitable for intended applications. The purpose of water pretreatment is to remove suspended and dissolved solids, dissolved gasses and other materials that can cause problems and that cannot be cost-effectively controlled by internal chemical treatment.

Water pretreatment has a tremendous effect on the reliable and efficient operation of boiler, cooling and process water systems. Without effective pretreatment, chemical treatment would be either ineffective or too costly. Since there are limitations on what chemical treatment alone can do, such as handling very high suspended solids or high hardness waters, external treatment systems are installed to remove the contaminants or reduce them to levels that can be effectively treated.

Pretreatment systems must be designed to meet specific on-site needs. Water used for cooling system makeup may be simply chlorinated if it is otherwise good quality water. However, in many large cooling systems, the makeup may be chlorinated, clarified and filtered and sometimes zeolite-softened. Water used for high pressure boiler feedwater will be further processed through reverse osmosis or demineralization, depending on the pressure. If returned condensate is contaminated, it may be treated by a suitable combination of these processes to bring the condensate back to feedwater quality. This is called condensate polishing (see chapter 3).

The terms *quality* and *purity* are used throughout this manual, and are sometimes assumed to be interchangeable. They are not. Purity is a quantitative term that defines the amount of impurities of all types in a water. Quality is a qualitative term defining suitability for use. For example, a surface water supply may be good quality for cooling tower makeup, but poor quality, requiring pretreatment, for use as boiler feedwater (more on this in chapter 1.)

There are many complex factors involved in the effective operation of external treatment systems. If the systems are not run effectively, system corrosion and fouling, unscheduled downtime, loss of production and wasted energy will occur. A basic understanding of these processes is therefore required in order to design and operate good internal cooling and boiler water programs. Improvements to external treatment operations can result in cost savings such as reduced regeneration chemical use, higher cycle boiler and cooling system operations, reduced needs for operator attention, cleaner boiler and heat exchanger surfaces, and reduced waste disposal costs.

Pretreatment processes are mostly mechanical. However, chemicals such as resin cleaners, high molecular weight polymers for clarification and cold lime softening, and reverse osmosis (RO) pretreatment chemicals are essential for effective operation of these processes. Many water treatment companies provide ion exchange resins and RO membranes as part of their total water treatment service.

The following sections are included in this chapter:

- Aeration - This section includes principles of aeration and data for carbon dioxide, ammonia and hydrogen sulfide removal.
- Clarification - Included are reaction chemistry with various chemicals used for clarification, description of various types of equipment and monitoring requirements.
- Precipitation Softening - Description of chemical reactions in hot and cold softening processes, troubleshooting and monitoring needs are in this section.
- Filtration and Adsorption - The different types of filtration equipment and media, such as down-flow, up-flow, Lamella, high efficiency 0.5 micron, mixed media, chlorine and organic removal principles, expected performance and typical operating parameters and troubleshooting are discussed.
- Reverse Osmosis – Principles of reverse osmosis, types of RO systems and membranes, pretreatment required and monitoring, such as the use of SDI (silt density index) and troubleshooting are in this section.
- General Ion Exchange Information - Principles of ion exchange, selectivity of resins for different ions, reactions and characteristics of various types of resins, vessel inspection and interpretation of resin analyses are included.
- Sodium Zeolite Softening - Principles of operation, hydraulic design, control tests and troubleshooting, including a discussion of brine elution studies, are found in this section.
- Demineralization - Principles and reactions of strong, weak, acidic and basic resin processes are included, as well as a discussion of equipment and operational steps, hydraulic design data and troubleshooting information.

- Condensate Polishing - Different types of condensate polishing equipment and the purpose of each process is included.
- Electrodeionization – A process that uses semipermeable membranes and electrical potentials to demineralize water without the need for chemical regenerants.

Each section includes system descriptions and illustrations to help explain the way in which the equipment is designed to work and the key operating principles of the processes. Details of the chemistry involved and typical design and operating parameters for each unit process are explained. Also included is testing that should be done to effectively monitor each process, plus equipment and trouble-shooting checklists to assist in obtaining more effective results.

1.2 THE AWT BOILER PRETREATMENT MATRIX

Following is an external treatment matrix that summarizes key factors (effect on water, control tests, service checkpoints, design data, ease of operation and pertinent comments) for many of the external treatment processes. This was prepared by the external treatment committee of AWT and is a very useful reference tool to select or evaluate the best pretreatment option for a system.

TABLE 2-1

The AWT Boiler Pretreatment Matrix

System	Effect on Water	Control Tests	Service Checkpoints	Design Flow	Ease of Operation	Comments
Sodium Zeolite Softener	• Replaces some cations: Ca, Mg, Fe, Ba, and Sr with Na. • Small increases in conductivity and TDS.	• Total Hardness: for influent = 50 ppm as $CaCO_3$, effluent = 0.1 • Influent of 500 ppm yields 1.0 ppm and influent of 1000 ppm yields 2.0 ppm	• Check influent and effluent for total hardness - test during service cycle and at end of a service cycle. • Check after all valves to detect hard water bypass leaks. • Check & record unit capacity between regenerations.	2-4 gpm/ft^3 2-14 gpm/ft^2	• Simple to automate and operate. Testing and monitoring also easy. • Run elution studies to check performance.	• High TDS & hardness waters have higher levels of leakage. • Effluent hardness is also influenced by the amount of salt used during regenerations. • Uses strong acid cation resin.

System	Effect on Water	Control Tests	Service Checkpoints	Design Flow	Ease of Operation	Comments
Sodium Chloride Dealkalizer	• Replaces some anions: HCO_3, SO_4, NO_3, for Cl. • Alkalinity reduction is about 90%. • It can significantly increase chloride, conductivity & TDS.	• Total Alkalinity: Regenerate when effluent alkalinity is >10 - 20% of the influent alkalinity.	• Check influent and effluent for total alkalinity. • Test during service cycle and at the end of a service cycle. • Check after all valves to check for any makeup water bypass leak. • Check and record unit processing capacity between regenerations.	2-4 gpm/ft^3 2-14 gpm/ft^2	• Simple to automate and operate. Testing and monitoring also easy.	• Must be proceeded by softening. • Capacity is affected by tot exchangeable anions. • High influent chlorides reduces alkalinity reduction • Higher capacity obtained when caustic is used along with salt. • Uses strong base anion resin. • Adding a small amount of caustic to regenerant brine enhances alkalinity removal
Acid Dealkalization / Decarbonation	• Reduces alkalinity by injecting a strong acid such as sulfuric or hydrochloric acid. • Sodium zeolite softening in front of a process is common to obtain hardness reduction.	• Typically drop pH to <4.3 or to free mineral acidity (FMA) point. • Bicarbonates and carbonates are converted to carbonic acid. • Water is passed over decarbonator to strip off carbon dioxide. NaOH is added back to raise pH and is controlled by a pH controller.	• Check pH after acid addition to achieve <4.3 pH & 0 alkalinity. • Check for CO_2 after decarbonator and before pH adjustment - should be < 10 ppm. • Test pH after NaOH addition for desired pH.	Flow design will be based upon the in-line static mixer for the acid and the design limitations of the decarbonator.	• A relatively low cost alternative for highly alkaline waters. •The operation is relatively easy to operate with a good setup, but requires acid & caustic handling – and upsets can be very damaging to downstream piping and boilers.	• Excellent monitoring equipment is needed with frequent manual checks to avoid problems.

System	Effect on Water	Control Tests	Service Checkpoints	Design Flow	Ease of Operation	Comments
Weak Acid Ion Exchange	• Replaces hardness associated w/alkalinity with hydrogen ion – and thereby reducing HCO_3.	• Hardness in effluent should equal the influent non-carbonate hardness. • When alkalinity in the effluent exceeds 10% of the influent alkalinity the unit should be regenerated.	• Test for influent and effluent for total alkalinity & hardness. • Check after all valves to detect makeup water bypass leaks. • Check and record unit processing capacity between regenerations.	1-3 gpm/ft^3 2-8 gpm/ft^2	• Simple to automate and operate. Testing & monitoring also easy. • HCl or H_2SO_4 acid used to regenerate, so there may be need for pH neutralization of the regenerate.	• A decarbonator is commonly used after the weak acid vessel to release the carbon dioxide created. • Weak acid units are very efficient in the use of acid, around 90%. • Could be used with a cooling tower to take advantage of pH depression
Split Stream Softening	• Lowers hardness, alkalinity, and TDS. • The alkalinity reduction is dependent upon how much water is directed to the sodium regenerated SAC unit and how much is direct to the acid regenerated SAC unit.	• Total Hardness: 0-1 ppm • Hydrogen unit alkalinity = 0, or operate with FMA. • Total alkalinity of blend: desired level below that of influent alkalinity. • Check CO_2 after decarbonator for blended water <10 ppm	• Same as for sodium zeolite softeners.	2-4 gpm/ft^3 2-14 gpm/ft^2	• Requires control to maintain the proper blend to achieve desired alkalinity.	• Applicable for high hardness and high alkalinity water.

System	Effect on Water	Control Tests	Service Checkpoints	Design Flow	Ease of Operation	Comments
Separate Bed Demineralizers	• SAC resin replaces all cations for hydrogen ion. • Lowers pH by converting all salts to their acid form. • SBA resin replaces anions with OH ion resulting in low conductivity • Final effluent generally <15 µS.	• Total hardness = 0-0.1 ppm. • pH: 5-7.5 • Conductivity: <15 µS/cm • Silica: <0.2 ppm	• Check for sodium leakage in the effluent. • Check for leaking valves of raw water into effluent. • When sulfuric acid is used for regeneration a two step addition may be required to avoid calcium sulfate precipitation on the resin. • Check and record unit processing capacity between regenerations.	• SAC: 1-4 gpm/ft^3 2-14 gpm/ft^2 • SBA: 1-4 gpm/ft^3 2-14 gpm/ft^2	• Moderately easy to operate. More difficult and more operator time if manual regenerations are required. • For silica rejection a heated caustic may be used. • Final pH neutralization may be required.	• A decarbonator may be used between the cation unit and the anion unit to remove CO_2 to reduce load on the anion unit. • Does not remove colloidal silica, only active silica.
Mixed Bed Demineralizers	• SAC and SBA resin mixed together in the same vessel. The close proximity yields higher purity water. • Conductivity < 0.25 µS.	• Conductivity: 0.05-0.25 µS/cm • Resistivity: 4-18 MΩ-cm. • Silica: 0.01-0.05 ppm • pH: 7	• Check influent and effluent conductivity/ resistivity and silica. • Check and record unit processing capacity between regenerations.	5-8 gpm/ft^3 10-20 gpm/ft^2	• Moderately complex to operate, but more simple when automated.	•Does not remove colloidal silic only reactive silica. • Silica will break through first accompanied by a temporary drop in conductivity.
Continuous Deionization (Not Reversal)	• Used as a polishing step, it can get resistivity to 16 MΩ-cm. • Often based on water qualities levels of 16 MΩ-cm can be guaranteed, some values to18 MΩ-cm	• Conductivity: 0.05-0.25 µS/cm. • Resistivity: 4-18 MΩ-cm. • Silica: 0.01-0.05 ppm • Need to monitor inlet total hardness, very low levels will result in scaling • ΔP on concentrate loop for scale buildup	• Amp draw monitoring vs. Quality • Concentrate loop ΔP • Stack unit flow • Temp	• Typically 7.5-15 gpm per stack (on EDI system) can get as high as 20 gpm on some designs • Low flow range is due to sufficient supply of water flow to cool preventing overheat. • Typical max temp 30-35°C	• Typically very hands off with proper pretreatment, neglecting pretreatment targets will cause you pain and reduced quality/flow with higher cleaning frequency. • With adequate pretreatment cleaning frequency can be every 6 months if not longer.	•Only remove ionizable materia colloidal silica not removed. • Very sensitive to hardness. • If supply water is very p may require brine injection on concentrate loop to help with amp draw • Should install protection cartridge filter upstream to prevent debris or solids from getting to unit, as they can not b backwashed.

System	Effect on Water	Control Tests	Service Checkpoints	Design Flow	Ease of Operation	Comments
Reverse Osmosis	• Rejects up to 99.9% dissolved solids, all suspended solids, and most organic compounds >70 molecular weight. • Does not reject dissolved gases. • Two pass RO can get dissolved solids to <1 ppm when the first pass feedwater is <1000 ppm. • Removes colloidal silica.	• Control tests set for each machine: feedwater characteristics and the membrane used. • Test results are used to determine when to clean membranes or to replace them. • Permeate conductivity, ΔP of each stage, normalized permeate flow. • For PA membranes, 0 ppm free chlorine.	• Test FW free chlorine, conductivity & pH. • Test, Log & Determine: feed pressure, the intermediate stage pressure/s, permeate conductivity, % salt rejection, normalized permeate flow, the ΔP's for each stage.	• Depends upon application, design and membranes used. • Flux rate: 5-8 gfd for wastewater, 8-14 for surface water, 14-18 for well water, 20-30 for second pass using permeate. • Typical % Recovery is 75%, meaning 75% of the feedwater leaves as permeate and 25% as reject or concentrate.	• Can be relatively easy to operate and automate to operate with minimal operator attention. • Cleaning frequency is dependent upon design and feedwater quality. • Frequent cleaning requirement can complicate operation. • Cleanings are triggered by 10-15% change in pressure drop, normalized permeate flow, and percent salt rejection.	• The key to successful RO applications is proper design, adequate pretreatment to yield acceptable feedwater characteristics of low good SDI, and proper monitoring followed by timely and efficient cleanings. • Pretreatment such as dechlorination and filtration ma be required upstream of RO. Can be preceded by softener o for some applications, followed by a softener.
Hot Process/ Anthracite Filter/Hot Zeolite	• Hot process reduces hardness, alkalinity, iron, manganese, silica & TDS. • When followed by a hot zeolite, final hardness is <1 ppm.	• After filters for hot process effluent, tests depend upon what chemicals are used. • If both lime & soda ash are used: • 2P-M = 5-10 ppm; • M-H = 30-50 ppm; • Hardness and Total Acidified Hardness - Hot Zeolite Softener: <1 ppm. • Sludge blanket level is controlled.	• Test total acidified hardness before and after anthracite filters to test for carryover. • Sample hot process vessels at different levels to control sludge blanket level.	• Depends upon application and design.	• Complicated and generally requires high operator attention. • Not good for intermittent operation.	• Control becomes much more difficult with changing makeup water characteristics and flow fluctuations. • Coagulants can enhance operation (e.g., sodium aluminate, polymers).

System	Effect on Water	Control Tests	Service Checkpoints	Design Flow	Ease of Operation	Comments
Mixed Bed Condensate Polisher	• Removes ionic & suspended impurities. • Reduces MU water needs & saves energy since it is already heated.	• Conductivity: 0.05-0.25 µS/cm on mixed bed resin	• Resin level check & proper interface on regeneration; low water volume (just above resin) on air scour mix step to avoid rapid bed expansion and internal lateral damage, as well as promotes good mixing. • Resin sampling in high temp operation due to impact on anion resin life. • Check & record unit processing capacity between regenerations.	25-35 gpm/ft^2	• Focus on intended removal needs, many used as iron filters only, however this indicates possible treatment issues in condensate that are better addressed by treating cause not the effect. • Can operate as SAC resin only, using an amine regeneration media to avoid pH depression.	• Relatively difficult regeneration, prone to iron fouling. • Temperature limited, some resins degrade in the presence of oxygen at temperatures as low as 100°F. • There are many other types of condensate polishers such as iron filters, softeners, media filters, magnetic filters, etc.

System	Effect on Water	Control Tests	Service Checkpoints	Design Flow	Ease of Operation	Comments
Deaerator: Spray & Tray Types	• Removes dissolved gases such as oxygen, carbon dioxide, and hydrogen sulfide. • Raises water temperature	• Dissolved oxygen: <7 ppb per Mfg. Specs for properly operating units (Chemetrics or Hach tests). May see 5-25 ppb for tray type & 20-40 ppb for spray type. • Indirect Testing: O_2 Scavenger residual + Scavenger usage DA Water Temp = 212 + 2*(DA psig) If scavenger usage steadily increases, to maintain boiler or FW residuals for no apparent reason (i.e., no change in steam load), then there may be issues with DA efficiency (broken nozzle, loss of trays, wrong operating temp or pressure). Also check condensate for oxygen.	• Monitor operating pressure & temp to make sure the DA is within manufacturer's operating specifications. • When testing for DO, sample at/after the storage tank. • Vent plume should be 2-3 feet high or with a 4-6 inch clear gap between the end of the vent pipe & beginning of the visible plume. • DA dome water temp should be within 4°F of the steam temp for the operating pressure; & the storage section should be within 5°F of the steam temp for the operating pressure.	• Depends upon style/type of DA. • Spray and Tray type DA's will have the spray nozzles and trays/fill located in a small chamber above the storage vessel. • Spray types tend to spray directly into the storage vessel.	• Easy to operate. • Should record operating temperature and pressure on a routine basis. • DA efficiencies should be determined for each account.	• Deaerators are typically elevated in boiler rooms to help create head pressure on pumps located lower. This allows hotter water to be pumped without vapor locking should some steam get into the pump. • Sometimes DA's are lined to help prevent corrosion. • Vent condensers can be used to improve DA efficiency. • Oxygen scavenger feed point is to the DA water storage section. • pH control may be required in FW tanks for high purity makeup applications.

System	Effect on Water	Control Tests	Service Checkpoints	Design Flow	Ease of Operation	Comments
Economizers	• A boiler economizer is a heat exchanger that heats feedwater, return water and/or other process fluid using hot stack gas from the boiler. • Capturing stack gas heat reduces fuel requirements for the boiler and equates to money savings as well as lower emissions due to the higher operating efficiency.	• Dissolved oxygen: 0 ppb • An oxygen scavenger residual is desired.	• Visual inspection during outages: check for cold end corrosion.	• There are various designs available depending on the manufacturer. • All are heat exchange vessels with flue gas on one side and FW/process fluid on the other.	• Relatively easy to operate.	• Cold end corrosion is an issue with these units. This occurs when temps drop to the acid dew point: 240-280°F, depending on sulfur content in stack gas. • Oxygen scavenger should be feed upstream w/a positive residual carried through the unit.

System	Effect on Water	Control Tests	Service Checkpoints	Design Flow	Ease of Operation	Comments
Feedwater Heaters	• Preheating feedwater reduces the amount of energy needed to make steam and, thus reduces plant costs of operation. It also improves the thermodynamic efficiency of a system and helps to avoid thermal shock to the boiler metal when FW is introduced back into the steam cycle. • Used primarily in the power industry. • Typical FW heater designs are open or closed. A closed design is similar to a shell and tube heat exchanger, with turbine extraction steam and hot drains supplying the shell side and boiler FW on the tube side. An open design is a direct-contact heat exchange in which extracted steam is allowed to mix with the feedwater.	• Eddy current testing for corrosion. • Sulfite testing may be conducted to ensure adequate chemical deaeration.	• Monitor feedwater temperatures. • Visually inspect during outages.	• Depends upon the size and type of FW heater. • Typical closed design is similar to a shell and tube heat exchanger	• Units relatively easy to operate.	• FeFeedwater heaters are not a replacement for deaerators – that both heat the water and deaerate the water. • FW heaters primarily add heat to feedwater w/minimal mechanical deaeration taking place.

A glossary of terms and references for further reading are included in section 12 of this chapter.

2.0 Aeration

2.1 INTRODUCTION

Aeration is the process of contacting water with air to remove undesirable gases and to convert certain metals to insoluble forms so as to permit their removal by subsequent filtration and other processes. This is usually accomplished by directing the water downflow countercurrent to the air flow, which may be atmospheric or forced-draft. The air-water ratio (standard cubic feet/minute per gallon/minute) must be sufficient for equilibrium to be established.

Aeration is used for the following:

- Oxidation of iron and manganese found in many well waters (oxidation tower),
- Ammonia and hydrogen sulfide reduction (stripping), and
- Carbon dioxide reduction (decarbonation).

2.2 PRINCIPLES OF AERATION

Aeration is a mechanical process for providing intimate contact of air with water. As applied to water treatment, aeration transfers gas molecules, most notably oxygen, from air (gas phase) to water (liquid phase). While dissolving oxygen in water is most often the goal, aeration also includes removal of undesirable gases, such as carbon dioxide, from water, sometimes referred to as degasification.

By far the greatest use for aeration is in the field of biochemical oxidation of organic wastes, domestic or industrial. But, aeration is also used extensively for oxidation of inorganic impurities such as iron, manganese, and hydrogen sulfide, and for removal or oxidation of volatile impurities causing odor or bad taste. Aeration simply to increase oxygen content of water is sometimes carried out as the last step in a water or waste treatment plant.

Aeration proceeds in three separate steps:

(1) Air is brought into intimate contact with water by exposing a large surface area. This is created mechanically in the form of many drops or small bubbles, depending on the type of aerator.

(2) Gas molecules pass across this surface into the liquid phase. The gas must pass through a thin barrier at the liquid surface, a liquid film, before it reaches the bulk of the liquid phase. The liquid underneath the film quickly becomes saturated with oxygen, and

(3) Gas molecules diffuse away from the liquid film into the bulk of the liquid until saturation is complete.

2.3 IRON AND MANGANESE OXIDATION

The objective in aerating water containing iron and manganese is to saturate the water with oxygen, in order to promote oxidation of ferrous and manganous ions to insoluble forms that can be filtered. Thus, ferrous bicarbonate reacts with dissolved oxygen and water to form red insoluble ferric hydroxide, as shown in equation (2-1):

$$4Fe(HCO_3)_2 + O_2 + 2H_2O = 4Fe(OH)_3\downarrow + 8CO_2\uparrow \qquad (2\text{-}1)$$

Similarly, manganous bicarbonate forms insoluble black manganese dioxide:

$$2Mn(HCO_3)_2 + O_2 = 2MnO_2\downarrow + 4CO_2\uparrow + 2H_2O \qquad (2\text{-}2)$$

The ferric hydroxide and manganese dioxide are removed by filtration or other processes, following aeration. The oxidation of both iron and manganese occurs fastest at a pH over 8.0. Theoretically, 1 mg/L of oxygen will oxidize 7 mg/L of Fe^{2+} or Mn^{2+}, but excess air is required to drive these reactions to completion.

2.4 REMOVAL OF DISSOLVED GASES

2.4.1 Stripping Mechanisms

As explained in Chapter 1, the solubility of any gas in water obeys Henry's Law, which states that the solubility is proportional to the partial pressure of the gas in the atmosphere in contact with the liquid surface. Another way of saying this is that a gas dissolved in water is in equilibrium with the same gas in the vapor space above the liquid. If the concentration of this gas in the vapor space decreases, gas will leave the liquid to reestablish equilibrium.

This is the basis for removal of dissolved gases from water by a process called "stripping". Examples are removal of ammonia from waste water by air stripping, and removal of dissolved oxygen from boiler feed water by steam stripping in a deaerator. Since air does not contain ammonia, and good quality boiler steam does not contain oxygen, bubbling air or steam through water causes ammonia or dissolved oxygen to transfer from the water to the gas phase. Dissolved oxygen removal, as part of boiler feedwater preparation, is covered in chapter 3 of this manual.

2.4.2 Effects of Temperature, Pressure and pH on Stripping Efficiency

Since gases are inversely soluble in water (chapter 1), the stripping process can be made more efficient by heating the water. In a properly designed and operated deaerator, for example, the concentration of dissolved oxygen in the water can be reduced to as low as 7 parts per billion (ppb) as explained in chapter 3.

Referring again to chapter 1, some gases react with water, while others do not. Oxygen and nitrogen do not react with water, so that their solubilities are controlled by the temperature of the water, and the partial pressure of oxygen or nitrogen in the gas phase in contact with the water.

Other common gases, such as carbon dioxide and ammonia, react with water and ionize to form acidic or basic solutions. These are called hydrolysis reactions, as explained in chapter 1:

$$CO_2 + H_2O = HCO_3^- + H^+ \qquad (2\text{-}3)$$

$$NH_3 + H_2O = NH_4^+ + OH^- \qquad (2\text{-}4)$$

Other gases, such as hydrogen sulfide, ionize in water without reacting directly with the water:

$$H_2S = H^+ + HS^- \qquad (2\text{-}5)$$

As the equations show, these are reversible equilibrium reactions. The unionized gases can be stripped, but the ionized forms – bicarbonate, ammonium and hydrosulfide ions – are not volatile and can not be removed by stripping. Thus, for example, adding acid to an ammonia solution (equation 2-4) neutralizes the hydroxide ions and pulls the equilibrium to the right, forming more ammonium ions. Hence, ammonia can not be stripped from an acid solution. Stripping efficiency can be increased by raising the pH – that is, adding more hydroxide ions to force the equilibrium to the left.

In a similar manner, carbon dioxide removal can be increased in a decarbonator by adding acid. Figures 2-1 and 2-2 show how pH affects the percentage of carbon dioxide and ammonia that can be removed by stripping.

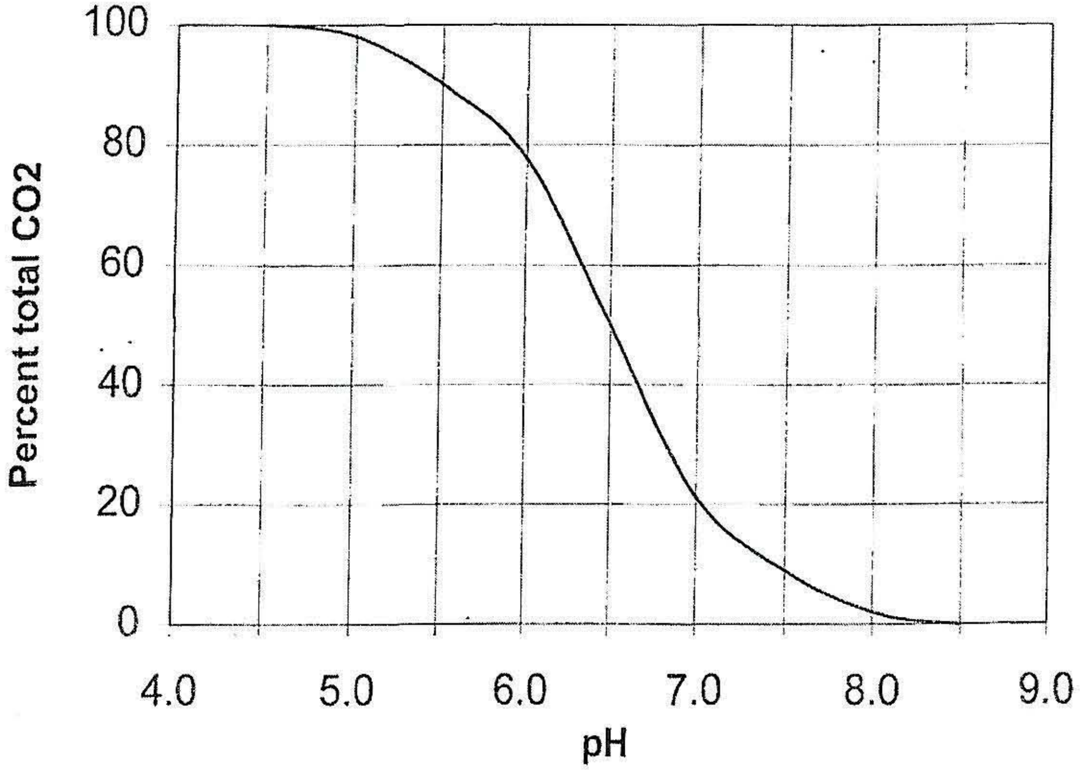


Figure 2-1. Percent carbon dioxide available for removal vs. pH at 77 °F.

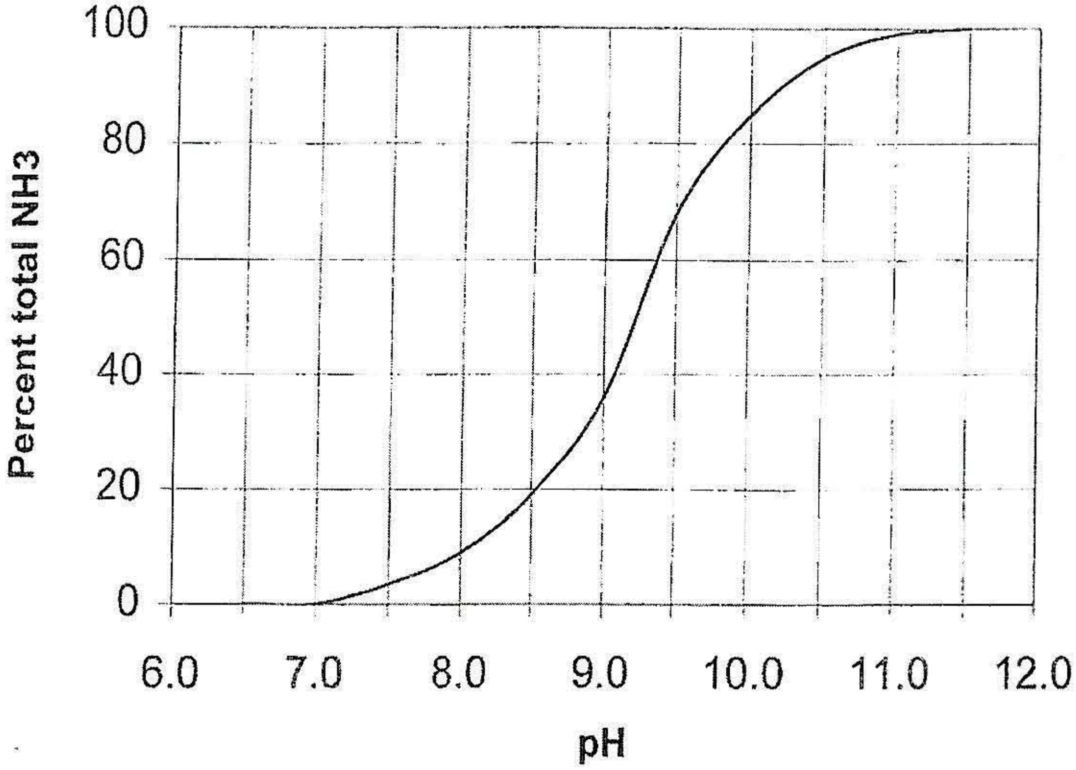


Figure 2-2. Percent ammonia available for removal vs. pH at 77 °F.

small particles into larger masses. Flocculant polymers can be cationic, anionic or nonionic, depending on the specific application.

By using organic polymers, it is possible to accomplish coagulation and flocculation without the requirement for precipitation of additional suspended solids from inorganic coagulants. Waters containing greater than 60 JTU turbidity may be treated with a primary coagulant polymer alone, determined by testing. With lower turbidity waters, bentonite clay may be added to help build floc. The clay provides additional surface area for adsorption of the solids.

Advantages of reduced use of inorganic coagulants include creating a reduced volume of sludge that is more easily dewatered. In addition, there is no effect on pH, less potential for metal (iron and aluminum) carryover and less addition of total dissolved solids to the water.

Dosage control is sometimes more critical with polymers than with inorganic coagulants. For example, it is possible to overfeed coagulation polymers that neutralize negative charges on suspended particles. This can cause charge reversal and resuspension of the solids.

3.2.3 Process Variables

In any coagulation process, raw water quality will have a considerable effect on the performance of the chemicals used. High turbidity increases the solids loading in the clarifier, whereas low solids content provides too few floc-forming nuclei. High organic content, detergents, and natural or synthetic dispersants tend to stabilize the colloidal suspension, causing higher chemical coagulant demand. Low bicarbonate alkalinity may necessitate pH adjustments. Gas formation caused by microbiological contamination may cause fouling of equipment and floc and interfere with settling.

Color reduction in clarification usually requires addition of chlorine and use of aluminum and iron salts. Optimum color reduction occurs at a lower pH than is normally required for turbidity removal.

3.2.4 Jar Testing

It is important to choose the proper chemical for the treatment of any water. The chemicals and dosages can vary from season to season and from day to day.

Selection of chemical programs for clarification systems is an empirical process that requires knowledge, experience and good judgment. Clarifiers are dynamic systems that require balanced control of flow-through rate, solids loading and chemical additions to maintain good solids removal. A change in any of these variables, or in the nature of the suspended solids, may require an immediate adjustment in the chemical program to maintain control. An experienced plant operator can tell from the solids carryover rate, the height and density of the sludge bed, sometimes even from the wind direction, when a change in polymer dosage is required.

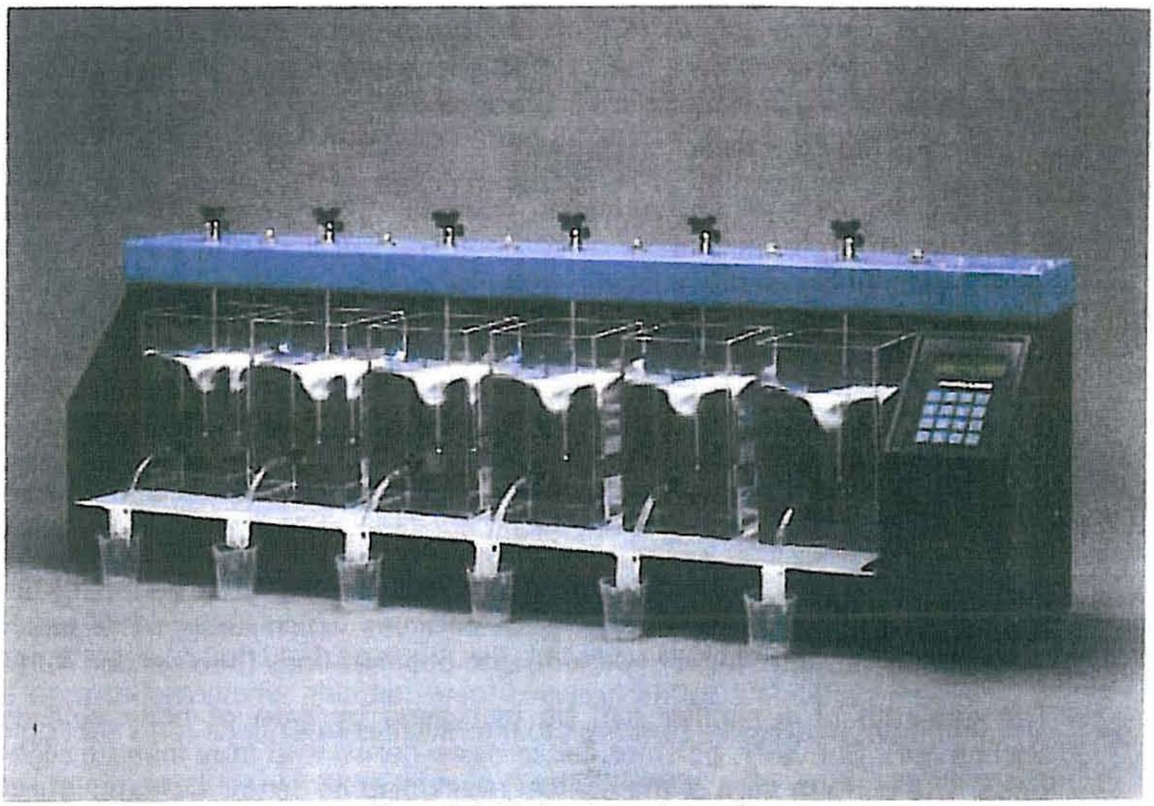


Figure 2-4. Modern jar testing equipment.

Figure 2-4. Modern jar testing equipment.

The standard method for choosing an effective chemical clarification program is jar testing (Figure 2-4). This test consists of placing samples of the water to be clarified in standard containers, usually one liter beakers, adding the proper amount of chemicals to be tested, mixing them using carefully controlled procedures and determining settling time, sludge density and supernatant water clarity. This permits appropriate estimates of:

- Performance of coagulants, flocculants and combination.
- Chemical dosages.
- pH level required for best results.
- Order of chemical addition and timing.

Section 1.01 Jar testing procedures must be modified to suit the demands of each site. A typical procedure running four to six parallel jars might consist of:

1. Premix time to establish uniform conditions in all jars: 3 – 5 minutes.
2. Add coagulant chemicals. Rapid mix for charge neutralization: 1 minute.

3. Add flocculant chemicals. Slow mix to build floc: 3 – 5 minutes.
4. Settling time: 5 – 15 minutes.
5. Record visual settling of floc and water clarity, measure supernatant turbidity.

Experience, careful control of the procedure, and comparison of test results with clarifier operations are the keys to successful use of jar testing to control chemical dosages in clarification processes.

3.3 CLARIFIER OPERATING VARIABLES

Key clarifier operating variables include: rise rate, temperature, pH, turbine/rapid mix speed, slow mix/flocculation zone, center well observations, rake speed, sludge blanket location, center well solids, and blowdown.

3.3.1 Rise Rate

A critical design feature in any clarifier is the rise rate. Rise rate is defined as the rate of water flow through a clarifier in relation to the surface area, usually expressed in gpm/ft^2 or occasionally as gpd/ft^2. Most influent clarifiers are designed to operate with rise rates from 0.75-1.25 gpm/ft^2.

Large, dense flocs can tolerate higher clarifier rise rates than small, light weight flocs, Thus, higher rise rates are usually specified for lime softening because calcium carbonate forms heavy dense particles which settle more easily than aluminum hydroxide, ferric hydroxide and polymer flocs (see section 4.0).

The rise rate of a clarifier can be increased by tube or plate settlers (see section 3.4). The surface area of the clarifier, excluding its center well and launders, is the effective available settling area.

3.3.2 Turbine/Rapid Mix Speed

The rapid mix zone in a clarifier is designed to encourage coagulant-particle collisions, for fast, effective charge neutralization.

The amount of agitation required for coagulation and flocculation with inorganic coagulants may not necessarily be sufficient with organic polymer coagulants. It may be necessary to increase the rapid mix speed or time when using a polymer. In some cases, external rapid mixing may be required. The primary coagulant polymer can be added to the suction side of the primary feed pump, to a rapid mix tank, or as far upstream in the system as practical.

Varying the speed of turbines or impellers can also draw sludge into the primary and secondary mix zones of the clarifier. This will provide intimate contact with recirculated solids in the mix zone, and furnish nuclei for more rapid coagulation and flocculation.

However, increasing the rapid mix too much can upset the sludge bed by pulling too much of the bed into the mixing area. The optimum mix speed and time must be determined separately for each unit and each chemical program.

3.3.3 pH

pH control is critical when metal coagulants such as alum or sodium aluminate are used. The pH range in which coagulation occurs is much broader with a polymer than with an inorganic coagulant. Also, the physical nature and size of the floc may change with the pH.

3.3.4 Temperature

Water temperature has several effects on clarifier and polymer performance. Cold water slows the chemical reaction rates and makes it more difficult for floc to settle through the more viscous, cold water. These problems can be partially overcome by providing additional mixing time or intensity and by feeding flocculants, which yield a denser, faster-settling floc. Changing temperatures can result in density differences, and rapid changes may cause upsets in the bed. Larger units are less prone to upsets, but all systems can be effected by temperature variations.

3.3.5 Slow Mix/Flocculation Zone Center Well Observations

Mixing is the most important variable in clarifier operations. Low turbidity waters require more mixing. Flocculation results from slow mixing in the secondary mix zone, allowing gentle particle-to-particle contact. The neutralized particles agglomerate into large settleable floc. The mixing speed must be adjusted for optimum particle contact without damaging the floc.

The clear water in the rivulets should be very clear. Cloudy water could signify an underfeed or overfeed of primary coagulant, as explained above. If floc looks poor and the water is still turbid, it may be necessary to adjust the primary coagulant dosage or mixing intensity.

3.3.6 Rake Speed

The rake pushes the sludge to a drawoff point where it is periodically removed as blowdown. This helps control the height of the sludge bed. Raising the rake speed will "fluff up" the sludge bed, while lowering the speed will "drop" the sludge bed. If the rake speed is too high, it can upset the bed, and if it is too low, it will decrease the contact between the newly formed floc and sludge solids. In either case solids carryover to the clarifier effluent can result.

3.3.7 Sludge Blanket Location

An adequate sludge blanket must be maintained to optimize solids settling and solids filtration in clarification. Most plants operate the clarifiers with 9-10 ft. of clear water above the sludge blanket. It is very important to know the sludge blanket level to maintain proper operating control.

3.3.8 Solids in the Centerwell

Slurry samples should be taken from the centerwell in most clarifiers. Place the sample in a graduated cylinder and record the settled volume after 5-10 minutes. As a guideline, good operation will have a settled volume of 10-25% of the total slurry volume.

3.3.9 Blowdown

Blowdown removes accumulations of settled floc (sludge). If the sludge bed becomes too high, severe floc carryover can result. Likewise, a low sludge bed caused by excessive blowdown will cause floc carryover. This is because there is little "filtering" effect through the sludge blanket or contact with the slurry.

Blowdown can be either manual or automatic. The blowdown interval is extremely important. Once the frequency of blowdown has been established, most plants will go to standard settings.

The blowdown sludge from the clarifier should be sampled on a regular basis. It is recommended that the sludge be analyzed to determine the total suspended solids (TSS) concentration. A typical level for sludge is 20,000 mg/L or 2% TSS concentration. Control in this range helps to ensure that a good sludge blanket is maintained without compaction or "setting up" of sludge in the clarifier.

3.4 CLARIFICATION EQUIPMENT

3.4.1 Horizontal Clarifiers

Horizontal clarifiers use separate chambers for rapid mixing, slow mixing, and settling. Primary coagulants are fed into the rapid mix chamber where charge neutralization occurs and pin point floc begins to form. Treated water then flows into flocculation chambers equipped with slow moving paddles. Flocculant aids are fed into this chamber to enlarge the floc and speed settling. The floc settles in the basin. Retention time is usually two to six hours and the rise rate is about one gal/min/ft^2. Horizontal units are usually found in larger plants. The units are relatively insensitive to flow rates. Costs limit their use in smaller installations.

3.4.2 Upflow Clarifiers

Relatively economical, upflow clarifiers process coagulation, flocculation, and sedimentation in one steel or concrete tank. These clarifiers are called upflow because the water flows countercurrent to the settling solids. This results in contact of turbidity particles with recirculated sludge and the sludge bed. These units maintain a high clarity effluent due to efficient use of chemicals and increased solids contact through internal sludge recirculation.

Because the retention time in an upflow unit is only one to two hours, upflow basins can be much smaller in size or holding capacity than horizontal basins of equal throughput. A rise rate of 0.75-1.25 gpm/ft^2 is normal for clarification.

Combination softening-clarification units can often operate at up to 1.5 gpm/ft^2 rates due to the larger particle size and higher densities of precipitated hardness sludge.

Although upflow units may provide more efficient sedimentation than horizontal designs, many upflow clarifiers vary speed of the rapid and slow mix sequence. Some types provide rapid mechanical mixing and rely on flow turbulence for flocculation. Others eliminate the rapid mix stage and provide only moderate turbulence for flocculation. In these systems, it is common practice to add the primary coagulant far upstream of the clarifier to provide added reaction time.

Most upflow designs are either sludge blanket or solids contact clarifiers (see below). Neither version can operate efficiently without adequate solids inventory in the clarifier. If sludge blankets or slurry pools are accidentally lost, upflow units will operate poorly until the sludge concentration is restored.

3.4.3 Sludge Blanket (Solids Contact) Clarifiers

After the coagulation and/or flocculation stage in a sludge blanket unit (Figure 2-5), the incoming water passes through a suspended layer of previously formed floc.

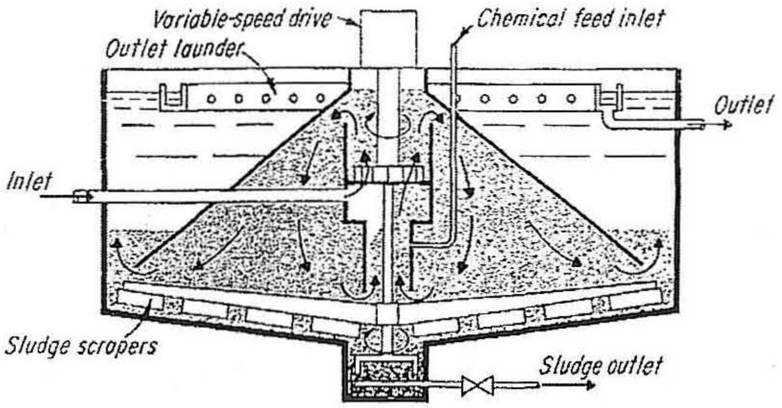


Figure 2-5: Sludge Blanket Clarifier

Because the center of these units is often shaped like an inverted cone, the velocity of the water decreases as it rises. When the velocity decreases enough to equal the settling rate of the suspended floc, a distinct solid/liquid interface forms. Normally, this interface, or sludge blanket, is carried as high above the bottom of the cone as possible without solids carryover. An excessive sludge blanket level is highly sensitive to changes in throughput, chemicals added, raw water chemistry, and temperature.

Effluent water clarity in a sludge blanket clarifier depends on the filtering action as the coagulated or flocculated solids pass through the already formed suspended floc. Higher sludge levels increase filtration efficiency.

If needed, coagulants are added to the influent water far ahead of the unit, to provide needed reaction time. Coagulant aids and flocculants are fed to the secondary (floc-forming) zone. The mixing zone uses a rotor impeller. It both mixes (rotor) and recirculates (impeller) the slurry and can be adjusted to allow a change in the ratio of mixing to recirculation without disturbing the slurry pool, which permits extremely flexible operation.

Solids contact units are built in several different designs in addition to the inverted cone design shown in Figure 2-5. Cylindrical center cone and rectangular clarifiers are common. Solids contact units can serve as both clarifiers and precipitation softeners (section 4.0). Bringing the incoming raw water into contact with recirculated sludge improves the efficiency of the softening reactions and increases the size and density of the floc particles.

3.4.4 Tube Settlers

Tube settlers are a series of sloped plates through which floc and clarified water pass in countercurrent flow (see Figure 2-6). Floc settles only a few inches from the surface of the plates, hits the plate surface, slides down, and concentrates in the bottom section of the clarifier. Settling distances are only a few inches or a few feet, rather than many feet.

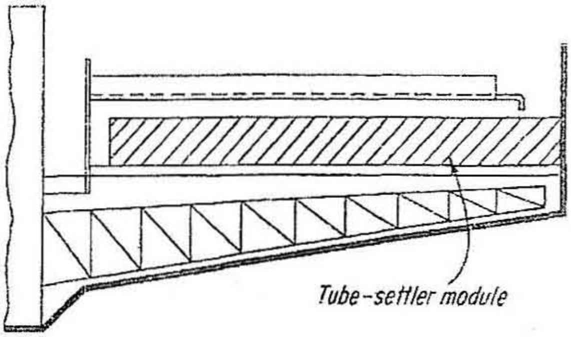


FIGURE 2-6 (Lamella or tube settling type clarifier)

Tube settlers can be installed in new or existing clarifiers. They reduce the overall area and retention time necessary to produce clarified water and can minimize convection problems caused by temperature changes. Tube settiers are capable of higher throughputs, with rise rates as high as 2 gpm/ft^2 compared to 1 gpm/ft^2 for standard clarifiers. This means that new units can be smaller, and existing units may use tube settlers to increase throughput.

If occasional high solids loadings occur or if sticky flocs are encountered, the tubes may clog. Water will short-circuit around the plugged tubes, restricting flow through the remaining few. Some units are designed with vibrator packs to shake the plates and prevent plugging. High pressure water flushing can also be used to clean the plates.

3.5 MONITORING CLARIFICATION PROGRAMS

Key control parameters are used to monitor clarification programs. Plant operators should regularly check and control these factors. Accurate logs should be kept to help in tracing and correcting problems with effluent water quality, sludge density and throughput. Following are some parameters that are normally noted – detail of logging will vary from plant to plant:

- Agitator speed
- Blowdown frequency
- Blowdown time
- Chemical feed - type and rate
- Chlorine residual
- Finished water pH
- Finished water turbidity
- Other parameters as required (color, hardness, etc.)
- Polymer solution strengths
- Rake speed
- Raw water flow rate and range
- Raw water pH
- Raw water turbidity
- Sludge blanket depth
- Temperature
- Sludge blanket time
- V_0/V percent solids

3.6 TROUBLESHOOTING CLARIFIER PERFORMANCE

Clarifier operating problems normally show up as floc carryover in the clear well. Table 2-3 lists possible operating problems and typical solutions. It is helpful for water treatment personnel to understand basic clarifier operations that affect choices of polymeric coagulants and flocculants, and application procedures.

Article II. TABLE 2-3: TROUBLESHOOTING CLARIFIER PROBLEMS

Problem	Possible Causes/Solutions
Floating floc or sludge	Air entrainment – make sure polymer pump is not sucking air, inject polymer below water surface, air in influent water Possible overfeed of polymer – adjust dose
Floc carryover	Hydraulic overload or flow surges Thermal currents Short circuiting – check operations clarifiers internals (mixing baffles launder not level, etc.) use tracer dye Low density floc – increase flocculant dosage Loss of sludge bed or recirculation Sludge bed too high – decrease bed height Chemical feed problem – check pump settings, dosages
Turbid water between floc in centerwell	Insufficient primary coagulant dose – increase dose Too much shear is tearing up floc – reduce agitation to change chemical feed points Overfeed of anionic polymer – decrease dose
Water layer above floc in centerwell	Flocculant overfeed – decrease dose Insufficient agitation – increase mixing
No floc in centerwell	Check to see if chemicals are being fed properly. Make sure sludge bed/recirculation has not been lost – increase recirculation, mixing slowly.

4.0 Precipitation Softening

4.1 INTRODUCTION

Basic water chemistry in chapter 1, especially including solubility, hardness, alkalinity and neutralization should be studied for fundamental chemistry knowledge before reading this chapter.

Precipitation softening is the conversion of soluble contaminants, primarily hardness, alkalinity and silica, to insoluble compounds that can be removed by mechanical separation, such as sedimentation and filtration. This process minimizes problems of mineral scale deposition in boilers and cooling systems, and provides water of acceptable hardness for many industrial processes.

In cold and hot process softening, hardness is removed by the precipitation of calcium carbonate and magnesium hydroxide. The precipitation is accomplished primarily by the addition of lime, caustic and soda ash. These chemicals may be used alone or in such combinations as lime and caustic, lime and soda ash, and caustic and soda ash.

Cold process softening is normally carried out at ambient temperature, and hot process temperatures are usually maintained between 212°F – 250°F. Waters with hardness and alkalinity levels between 150 to 500 mg/L as calcium carbonate have historically been softened by precipitation methods. Due to capital costs, space problems and sludge disposal concerns, newer membrane-based and ion exchange technologies are replacing precipitation softening, especially for boiler water make up. Hot process softening is mostly of historical interest and will not be covered in detail in this manual. Few new cold process softeners are being built, but the process is still important and should be understood.

4.2 PRINCIPLES OF PRECIPITATION SOFTENING

Precipitation softening is a straightforward application of the principles of carbonate alkalinity, hardness and solubility discussed in chapter 1 of this manual.

Generally, water supplies available from natural sources contain alkaline and neutral salts of calcium, magnesium, sodium, potassium, and in some instances, lower levels of iron, manganese, barium and aluminum. Additional contaminants can include higher concentrations of dissolved solids, silica and organic matter.

Hardness in water is usually classified as temporary hardness or permanent hardness:

- Temporary hardness is defined as the amount of calcium and magnesium in the water, expressed as calcium carbonate, that is equivalent to the carbonate alkalinity, also expressed as calcium carbonate. Temporary hardness is also known as "carbonate hardness" or "alkaline hardness."

The term 'temporary" derives from the fact that temporary hardness can be removed by boiling the water. This converts bicarbonate ions to carbonate and lowers the solubility of calcium carbonate (see chapter 1).

- Permanent hardness is defined as the excess calcium and magnesium in the water above the amount classified as temporary hardness. This excess calcium and magnesium is usually present as chloride, sulfate, nitrate and fluoride salts. Permanent hardness is also known as "non-carbonate hardness" or "non-alkaline hardness." Permanent hardness can not be removed simply by boiling the water.

4.2.1 Lime Softening

The basic lime softening process involves the addition of quicklime (calcium oxide, CaO) or slaked lime (calcium hydroxide, $Ca(OH)_2$) to water to convert bicarbonate alkalinity to carbonate. The carbonate alkalinity precipitates both the temporary hardness in the water and the amount added as lime to insoluble calcium carbonate, as shown in equations 2-10 and 2-11:

$$CaO + H_2O = Ca(OH)_2 \qquad (2\text{-}10)$$

$$Ca(HCO_3)_2 + Ca(OH)_2 = 2CaCO_3\downarrow + 2H_2O \qquad (2\text{-}11)$$

The added lime or quicklime also removes any unionized carbon dioxide in the water, as in equation 2-12 (chapter 1):

$$CO_2 + Ca(OH)_2 = CaCO_3\downarrow + H_2O \qquad (2\text{-}12)$$

Finally, magnesium temporary (carbonate) hardness is removed by precipitation as magnesium hydroxide, which is substantially less soluble than magnesium carbonate (equations 2-13 and 2-14):

$$Mg(HCO_3)_2 + Ca(OH)_2 = CaCO_3\downarrow + MgCO_3 + 2H_2O \qquad (2\text{-}13)$$

$$MgCO_3 + Ca(OH)_2 = Mg(OH)_2\downarrow + CaCO_3\downarrow \qquad (2\text{-}14)$$

Lime will also remove any permanent magnesium hardness present in the water by direct conversion to magnesium hydroxide. This, however, creates an equivalent amount of permanent calcium hardness, as shown in equation 2-15:

$$MgSO_4 + Ca(OH)_2 = Mg\ (OH)_2\downarrow + CaSO_4 \qquad (2\text{-}15)$$

4.2.2 Lime-Soda Softening

Lime alone cannot remove permanent calcium hardness because it does not supply the needed carbonate alkalinity. Soda ash (sodium carbonate) is added to solve this problem by converting calcium sulfate to calcium carbonate:

$$CaSO_4 + Na_2CO_3 = CaCO_3\downarrow + Na_2SO_4 \qquad (2\text{-}16)$$

4.2.3 Other Chemicals Used in Lime Softening Processes

Some plants use caustic soda, usually supplied as 50% liquid sodium hydroxide (NaOH) in softening operations. Caustic reacts with carbon dioxide and bicarbonate to form soda ash for calcium non-carbonate hardness removal (equations 2-17 and 2-18). In most common water supplies, caustic can replace all the soda ash requirement but only part of the lime demand:

$$CO_2 + 2NaOH = Na_2CO_3 + H_2O \qquad (2\text{-}17)$$

$$Ca(HCO_3)_2 + 2NaOH = CaCO_3\downarrow + Na_2CO_3 + 2H_2O \qquad (2\text{-}18)$$

$$Mg(HCO_3)_2 + 4NaOH = Mg(OH)_2\downarrow + 2Na_2CO_3 + 2H_2O \qquad (2\text{-}19)$$

$$MgSO_4 + 2NaOH = Mg(OH)_2\downarrow + Na_2SO_4 \qquad (2\text{-}20)$$

Soda ash formed in reactions (2-17, 2-18 and 2-19) will react to remove permanent (non-carbonate) calcium hardness as in equation (2-16).

In some highly alkaline waters, where the total alkalinity is greater than the hardness, substantial quantities of sodium bicarbonate ($NaHCO_3$) may be present. The excess alkalinity may be reduced by the use of gypsum (calcium sulfate) to add hardness, as shown in equations 2-21 and 2-22:

$$2NaHCO_3 + Ca(OH)_2 = CaCO_3\downarrow + Na_2CO_3 + 2H_2O \qquad (2\text{-}21)$$

$$Na_2CO_3 + CaSO_4 = CaCO_3\downarrow + Na_2SO_4 \qquad (2\text{-}22)$$

4.2.4 Lime Softening Calculations

Using the principles of alkalinity and hardness as explained in chapter 1, and with all chemicals expressed as calcium carbonate, determining needs for lime and soda ash becomes a simple matter of addition and subtraction.

As one example, consider a water with the following composition:

Calcium hardness	75 mg/L
Magnesium hardness	25 mg/L
Alkalinity	50 mg/L

In terms of carbonate and noncarbonate hardness, this analysis amounts to:

Carbonate hardness	50 mg/L
Noncarbonate hardness	25 mg/L Ca as $CaCO_3$ 25 mg/L Mg as $CaCO_3$

Treatment requirements for lime-soda softening will be:

Carbonate hardness:	Ca:	50 mg/L lime (equation 2-11)
Noncarbonate hardness	Ca:	25 mg/L soda ash (equation 2-16)
	Mg:	25 mg/L lime (equation 2-15) 25 mg/L soda ash (equation 2-16)

through the filters. If the quality of the incoming water is such that the floc particles are too small or have little resistance to shear stresses, floc will penetrate completely through the filters. If pretreatment processes cause large quantities of strong floc (carryover) to reach the filters, there may be little floc penetration into the filters and very short filter runs will result.

5.3 FILTRATION SYSTEMS

5.3.1 Filter Media

The most common types of filters in use are gravity type and pressure type. Generally, the filtering medium used in these filters can be one of the following:

a) Sand

b) Anthracite coal

c) Dual media (coal + sand)

d) Mixed media (coal + sand + garnet)

Sand, sometimes graded in different mesh sizes, and anthracite coal are most common. The filtration medium is supported by different grades of gravel or coarse anthracite. These supporting layers are called "subfill." The gravel bed that supports the filter medium prevents fine sand or anthracite from passing into the underdrain system and distributes backwash water. This supporting bed consists of 1/8 to 1-1/2 inch gravel in graded layers to a depth of 12 to 16 inches. The suspended matter is entrapped within the voids of the filtering medium grains above the subfill.

The size and shape of the suspended particles govern the efficiency with which the filter media removes solids. The media must be coarse enough to allow sludge to penetrate the bed for two to four inches. Although most suspended solids are trapped at the surface, some penetration is absolutely essential to prevent rapid increase in pressure drop and blinding of the filter bed.

Sand and anthracite media for filters are rated by particle size and uniformity. Expected water quality depends on the influent water, type of filter and media. Table 2-4 shows typical effluent quality with different media. The actual performance of any filter system depends upon the design, capacity, operating conditions and influent water quality.

TABLE 2-4

Filter Performance Expectations

Media	Influent Solids mg/L	Effluent Turbidity JTU
Granular anthracite	5 – 50	<1
Sand	5 – 20	<1
Mixed anthracite/sand	5 – 50	0.1 – 1.0
Upflow anthracite/sand	2 – 25	0.1 – 0.5

The accumulating load of suspended particulate matter in the medium causes an increasing pressure drop across the filter during the filter run. When this loss reaches a predetermined limit, the filter is taken off line for cleaning. The filter is then cleaned by "backwashing" or reversing the flow from the bottom. By backwashing, the suspended matter is washed out of the filter. The backwash effluent may be collected for pumping back to the clarifier or softener, or it may be discharged to the sewer. The unit may also be backwashed on a timed basis. Backwashing is carried out at high flow rates that range from 10 – 20 GPM/ft^2, depending on the water temperature.

The rate of pressure drop increase during a filter run depends on the hydraulic loading (GPM/ft^2), the size of the filter media grains, and the amount and nature of the suspended matter removed from the water.

Water temperature affects filter performance due to viscosity. At 32°F, the viscosity of water is 44% higher than at 72°F. Backwashing effectiveness can improve with cold water, since higher viscosity water more effectively scours the bed to remove solids. Floc formation is much slower at low temperatures so the filterability at a given plant may vary seasonally. In the summer, floc may stay on the surface, but it may penetrate deeply into the filter in the winter.

5.3.2 Sand Filters

Gravity type filters are either rectangular or circular, and are made of steel, wood or concrete. They are open at the top and operate at atmospheric pressure. In the bottom is an underdrain collection system, which collects the filtered water and distributes the backwash water.

The original gravity filters were slow sand filters. These filters, utilizing sand with an effective size of about 0.2 mm, were designed to operate at very low flow rates such as 0.05 to 0.13 gpm/ft^2. Since slow sand filters required large areas and were costly to install, they were largely replaced by rapid sand gravity filters.

A rapid sand filter consists of sand on top of a gravel bed. A typical filter might have 24-30 inches of 0.35 – 0.6 mm effective size sand with a 1.2 – 1.8 uniformly coefficient. The sand has specific gravity of about 2.65. This filter is typically operated at 2 – 4 gpm/ft^2.

When backwashed, the finer sand grains end up on top. The top few inches of sand do the bulk of the filtering, which results in excellent water quality but short filter runs.

High efficiency sand filters (Figure 7) are commonly used in commercial installations and some are designed to removed particles smaller than 5 microns. Most cooling water particles are in the 0.5 to 5.0 micron size range. These filters have a small footprint and typically these type filters will require significantly less backwash water. Some designs use ultra fine sand for the top layer, with swirling water across the top to remove contaminants and minimize plugging. These filters are claimed to remove 80% of particles in the 0.5 to 5.0 micron size range with 50% removal in the 0.5 micron size and 80% in the 2.0 micron size.

FIGURE 2.7 High Efficiency Sand Filter

High efficiency sand filters for commercial applications are available from several manufacturers. Designs and removal efficiencies vary.

5.3.3 Dual Media Filters

A dual media filter (Figure 2-8) consists of anthracite coal on top of sand, sitting on a gravel support. A typical filter might consist of 20 inches of 0.8 – 2 mm anthracite with a specific gravity of 1.35 – 1.75 on top of 10 inches of 0.4 – 1 mm sand. It may be operated at 3 – 5 gpm/ft^2.

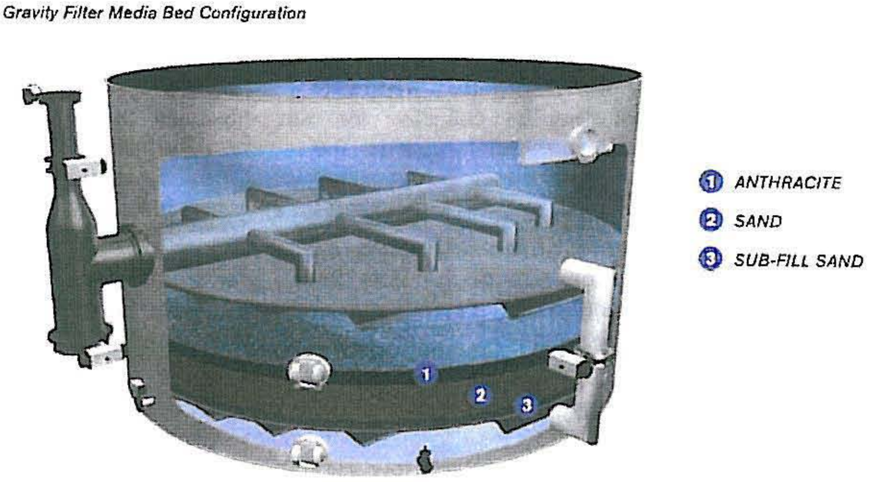


FIGURE 2-8

Dual Media Filter

In dual media filters, a coarse coal filter is on top of a fine sand filter, which allows deeper bed penetration and longer filter runs. The higher flow rate offsets the deeper bed penetration, and filter runs end up about the same as rapid sand filters. If head loss is a problem, the coal size can be increased. If turbidity breakthrough is a problem, the sand size can be decreased.

5.3.4 Mixed or Multi-Media Filters

Mixed or multi-media filters consist of anthracite on top of sand, followed by garnet on top of a gravel base. These filters can handle higher solids loadings, provide increased filter runs or be operated at a higher flow rate. A typical filter might consist of 18 inches of 1 – 2 mm anthracite on top of 8 inches of 0.5 – 1 mm sand with 4 inches of 0.2 – 0.4 mm garnet (specific gravity about 4) on the bottom. The gravel base is typically 4 – 6 inches deep. The flow rates are often 4 to 6 gpm/ft^2.

5.3.5 Pressure Filters

Pressure filters can be vertical or horizontal and the media can be sand or anthracite/sand. They are generally operated at a flow rate of 3 gpm/ft^2. Pressure filters are frequently used in industrial water conditioning. They require less space and can be placed in-line under pressure, thus eliminating double pumping. The main disadvantage of pressure filtration is that the filter effluent and medium cannot be readily observed.

5.3.6 Upflow Filters

Upflow filters are quite similar to in-line filtration in that a clarifier is not used to settle out the floc before filtering. However, these units can handle high solids loading (100 NTU or higher) at service flow rates of 5 – 10 gpm/ft^2. The upflow filter consists of two layers of sand on top of a gravel base. The finest sand is at the top of the filter and the coarsest at the bottom. Since the flow is up through the unit (from coarsest to finest sand) more of the bed depth can be used and high throughputs are possible. During the backwash cycle, air scour is used to help remove solids.

5.4 SPECIAL FILTRATION PROCESSES

5.4.1 Direct Or In-Line Filtration

With water having low turbidities (10 – 20 NTU), direct filtration can be carried out with, and at times without, the use of synthetic organic polymers. Many cooling water side stream filters are operated on this principle. The polymers act like filtration aids and form a microscopic film on the filter media grains. Removal of particulate matter occurs by deposition on this surface film. These polymers also increase the strength of the floc. Because of high velocity in the filter bed, the polymer may be added directly to the filter influent. Generally, these polymers are fed at very low dosage rates, usually less than 0.1 mg/1. However, for good results, the polymer dosages should be controlled precisely.

5.4.2 Precoat Or Septum Filters

Where suspended solids concentrations are very low, septum filtration can be used. These filters are often referred to as DE (diatomaceous earth) filters since this material is usually used as a filter precoat, although other filter aids can be used. The septum filter relies on a thin layer of precoat applied as a slurry to a porous septum to produce a filtering surface to strain the suspended solids. In most cases, water being filtered is pumped through the filter under pressure. In special designs, where low head loss is possible, the water may be pulled through using vacuum. As the filter becomes plugged, head loss increases and the solids, including precoat, have to be removed by reversing the flow through the unit. A new precoat is then applied and filtration is resumed. Usually, in addition to the precoat, a body feed of filter aid is used. This body feed is simply additional filter aid added to the influent to extend filter runs by continually providing a fresh filter surface. Because the filter aid has a different shape (morphology) than the solids in the water, the heterogeneous mixture is more permeable than the solids alone.

A relatively high ratio of filter aid to suspended solids is required to operate septum filters, making operating costs fairly high. Therefore, these units are not as common as granular media filters in most industrial systems. DE filters are often used for applications such as municipal swimming pools, and they are excellent for removal of oil from industrial plant condensate.

Septum filters can be cleaned of accumulated solids by air-bumping, a procedure requiring little or no water and producing a thick slurry or cake of accumulated solids. This simplifies solids disposal, and reduces backwash water requirements. They can also be fitted into a relatively small space, compared to granular media filters.

5.4.3 Microfiltration

Microfiltration is used where finer particle size removal is required for effective operation of certain systems. One example is quality of water required as influent to reverse osmosis systems. Microfiltration is generally effective at removing particles as small as 0.2 microns.

Typically cartridge-type filtration is used for this purpose and the units are replaced when needed, usually based on pressure drop. Microfiltration will remove suspended particles, bacteria and colloids to the size specified. Typical cartridge filters preceding an RO system have a 2 stage system of a 0.5-micron and a one micron size rating.

The filter media used initially was cotton string. Other compounds in common use include nylon and melt-blown polypropylene fibers. These are constructed as a depth filter design or as a pleated or triangular-pleated configuration.

There are also back-washable fibrous media depth filters. Another type of microfilter uses hollow fiber membranes. All water flows directly through the membrane and solids accumulate on the membrane surface. This type of system can use compressed air to expand the membrane wall to help flushing or "backwashing."

5.4.4 Ultrafiltration

Ultrafiltration is typically a cross-flow process (similar to reverse osmosis) that also removes organic matter. Five- to ten-percent of the inlet flow is used for the cross flow, which helps keep the surface from fouling. The principle and configuration are very similar to that used in reverse osmosis (see section 10 in this chapter).

5.5 BACKWASHING

5.5.1 Procedures

Backwashing of sand and multimedia filter beds is extremely important for removing the accumulated solids from the filter. Backwash water flows upward through the unit, suspending the medium and carrying away the solids. Surface or subsurface washes and air scours can help remove additional trapped solids. Backwash rates of 12 – 15 gpm/ft^2 are used for sand filters and 8 – 12 gpm/ft^2 for anthracite. Higher rates may be used for mixed media filters. Backwash rates are also temperature dependent. Higher rates are used at higher temperatures because the low density of the water decreases the uplift force.

Most problems encountered in filters are caused by improper backwashing. For example, mud balls are accumulations of solids not removed due to poor backwash procedures. As mud balls accumulate and compact, certain areas of the filter can become clogged and useless. Proper backwashing and internal design can avoid these problems.

Filter beds can become microbiologically active if they are not backwashed properly and kept clean. A contaminated filter bed can become a breeding ground for bacteria that can make microbiological control in the cooling tower difficult or impossible (see chapter 4). This problem can usually be corrected by backwashing the filter and then soaking it for several hours in a solution containing 10 mg/L or more of sodium hypochlorite or another oxidizing microbiocide (chapter 4). In severe cases, the only practical solution may be to replace the filter media.

5.5.2 Backwash Water Supply

The choice of backwash water supply is important. Filters on cooling towers are sometimes designed to use the circulating cooling tower water as backwash supply. This is a simple solution when a sufficient supply of fresh water is not available to support the required backwash flow rates. However, there are important disadvantages to using circulating water as backwash supply:

- Chemical treatment in the backwash water is lost and must be replaced in the circulating water. This can be costly, and If it is not done routinely, treatment may drop to seriously low levels (see chapter 4).
- Backwashing with tower water distributes a low level of suspended solids throughout the filter bed, including any microbiological contamination in the circulating water. Advantages of initial filtration with clean sand are lost and the filter bed can easily become microbiologically active (section 5.5.1.)

If a sufficient supply of fresh water for backwashing is not available, it is better to install a tank that can be used to store backwash water, rather than use tower water for backwashing. Similarly, if the available sewer or discharge piping can not handle the backwash water flow, the backwash water can be stored and discharged slowly while the filter is on line.

5.6 BAG AND CARTRIDGE FILTERS

As the names imply, bag and cartridge filters are simply housings containing woven cloth bags or cartridges that serve as the filter media. These filters are not backwashed; rather, when the media is saturated as shown by a rise in pressure drop across the filter, the filter is taken off line and the bag or cartridge is replaced. Figure 2-9 shows some common bag filter designs.

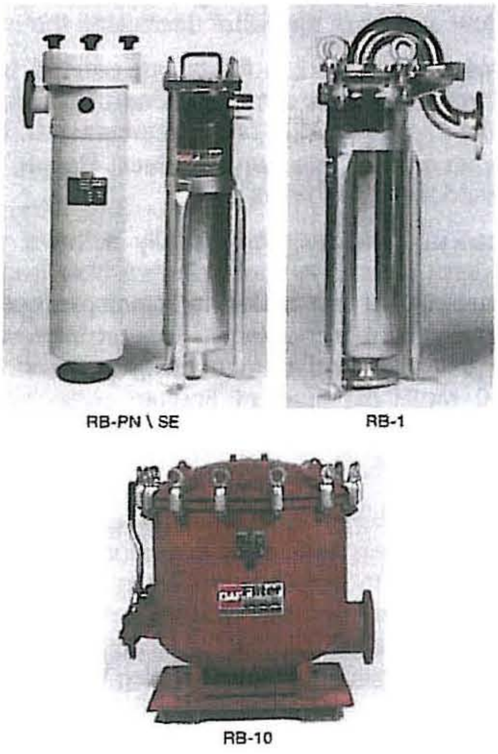


FIGURE 2.9

Common bag filter designs

Bag and cartridge media are available in a variety of materials and pore sizes to match application requirements. An advantage of these media is that when the filter is used to clean a contaminated system, coarse media can be installed at first, followed by smaller particle sizes as the suspended solids are removed.

Bag and cartridge filters are used on small systems; where backwashing is not practical; and on closed systems where even the small loss of system water during backwashing could be significant over time. Because the filter media are replaced regularly, these filters rarely become contaminated. By using banks of filters and rotating replacement operations, large systems can also be filtered in this way.

Disadvantages of bag and cartridge filters:

- The replacement operation is manpower intensive and can be expensive if the media are replaced frequently.
- Disposal of used media can sometimes be difficult, especially if the suspended solids being removed from the system are contaminated so that they constitute a defined hazardous waste.

5.7 ADSORPTION PROCESSES

5.7.1 Introduction

Filtration processes, as described in this section, are designed to remove insoluble – that is, suspended or colloidally dispersed – matter from water. Filtration has no effect on soluble impurities in water. However, some types of soluble impurities can be removed by a process similar to filtration, called adsorption.

Adsorption depends upon the tendency of organic molecules to become attached to reactive surfaces. Three types of attachment are possible:

- Physical adsorption: Many naturally occurring surfaces contain net positive and negative charges. Organic molecules are attracted to these surfaces and can be held there by physical processes similar to electrical attraction. No actual chemical reaction occurs, and physically adsorbed material can easily be removed by flushing (backwashing) the adsorbing surfaces with clean water.
- Chemical adsorption: In some cases, chemical reactions are involved. For example, many colored organic compounds contain acidic and basic groups. These molecules can adsorb onto surfaces that contain free carboxyl (acidic) or hydroxide (basic) groups, and react to form salts or esters (see chapter 1 for neutralization reactions). The resulting compounds are chemically bonded to the surface and cannot be removed by simply flushing with water.
- Destructive reactions: Some compounds in water can destructively attack the adsorbing surface, so that both the attacking molecule and the surface

material are destroyed. The best example of this is the use of activated carbon beds to remove chlorine residuals from water, forming carbon dioxide gas and hydrochloric acid (see section 5.7.2 below).

The two most widely used adsorbents in industry are activated carbon and activated silica. The term "activated" means that the materials are treated, usually by heating under controlled conditions or by acid treatment, to produce highly active, porous surfaces. Activated carbon and activated silica are used to purify water, industrial process fluids and products, and air. They are available as granular particles in equipment very similar to sand filters, or as powdered materials added directly to water or process fluids in batch reactions.

The information in this manual is restricted to the use of granular activated carbon for treating potable water, industrial makeup water and waste water.

5.7.2 Dechlorination

Chlorine in water reacts rapidly with carbon:

$$2Cl_2 + C + 2H_2O = CO_2 + 4HCl \qquad (2\text{-}23)$$

In this chemical reaction, 1 mg/L Cl_2 reduces the alkalinity of the water by about 1.5 mg/L (as $CaCO_3$) by the production of hydrochloric acid.

As explained above, this reaction destroys both the chlorine and the surface of the carbon bed. However, when granular carbon beds are used only for dechlorination service, the carbon's capacity is extremely high and no regenerative process is employed. Regular backwashing is usually adequate to remove any suspended matter filtered from the water by the carbon bed, any bacterial slimes that may have formed, and to expose fresh surfaces for contact with the chlorine.

In the beverage industry, many bottling plants use high chlorine dosages to ensure complete sterilization. If the residual chlorine were not removed, it would destroy some of the organic materials used for flavoring. In the distillery industries, free chlorine would be objectionable in the fermentation process. For these operations, carbon filters are ideal for removing tastes and odors and for dechlorination. Because the water has been pretreated, the organic loading is generally very low. Carbon beds may operate for several months to more than a year before exhaustion, and it is often more practical to replace the carbon bed with new material than to regenerate it.

Dechlorination is also an important wastewater treatment process where plant discharges are sent to a natural waterway. Activated carbon may be used here, especially if other materials, such as organic color bodies, must also be removed from the water. If only dechlorination is required, treatment with a reducing agent such as sodium sulfite may be simpler and equally effective.

Undesirable tastes and odors, which may be produced by chlorination of water, are also removed by carbon treatment.

5.7.3 Removal of Organic Matter by Adsorption

Surface water supplies may contain naturally occurring decaying vegetation, pollutants such as industrial wastes, surfactants, etc. The effectiveness of activated carbon for organic removal varies with molecular weight: higher molecular weight species are more effectively removed. Carbon will remove non-polar compounds such as chlorinated phenols and chloramines very effectively.

Dissolved organic matter in water can cause permanent fouling of anion exchange resins. Activated carbon beds upstream of the demineralizers protect the resins from organic fouling and also from damage caused by free chlorine in the water. Demineralization is discussed in section 8 in this chapter.

The ability and capacity of activated carbon to remove dissolved organic matter is determined by the properties and nature of the organic matter. When granular carbon is exhausted in this service, it is usually replaced with either new or thermally regenerated carbon.

5.7.4 Final Filtration

Granular activated carbon beds are used as final filters after clarification and sand filtration, when very clean water must be prepared. The carbon bed removes, by adsorption, small colloidal particles that pass through the sand filters, plus soluble organic color bodies and other molecules as explained above. In the same way, carbon beds are used as a final tertiary waste water treatment when very clean effluent is required.

5.7.5 Principles of Operation

Granular activated carbon is usually used in downflow vertical pressure filters that can be backwashed with water or exchanged as needed.

Table 2-5 is a summary of expected removal efficiencies of an activated carbon bed:

TABLE 2-5

Performance of Activated Carbon Filtration

Function	% Removal	Mechanism
Total organic carbon (TOC) removal	95+	Adsorption
Dechlorination	100	Chemical destruction
Suspended solids removal	50-100	Filtration

No chemicals are needed for activated carbon to perform properly. Lowering the pH below 7 improves chlorine removal by reducing ionization of hypochlorous acid (chapter 1).

5.7.6 Control Tests

Plant personnel and carbon supply companies may perform the following tests to monitor bed performance and determine remaining bed capacity:

- TOC (total organic carbon) in the effluent.
- Chlorine in the effluent.
- Higher than normal pressure drops indicate that the bed may be plugged and require backwashing.
- Iodine number – a titration test that can be performed by a plant laboratory or carbon supplier. New carbon typically has an iodine number greater than 750. As the carbon is exhausted, the number drops. Replacement is recommended below 500.
- Volatile material adsorbed on the carbon can be measured using a laboratory oven and a TOC analyzer. A typical volatile loading could be as high as 20% by weight. Replacement is recommended when volatiles exceed 15%.

6.0 Ion Exchange - General

6.1 INTRODUCTION

Ion exchange has been used for over 60 years to effectively pretreat water used for industrial and commercial processes. The primary purpose of ion exchange is to remove dissolved inorganic salts, such as hardness, silica, alkalinity, and other ions from boiler feed water in order to minimize scale and corrosion in boiler systems. Ion exchange methods are also used extensively to prepare very pure water for pharmaceutical, electronics and other industrial applications.

Ion exchange resins are naturally occurring or synthetic materials that have the ability to exchange one ion in a solution for another, hold the exchanged ion temporarily, and release it to a regenerant solution. These compounds are widely used to treat raw water supplies which contain dissolved salts. A proper exchange and regenerant system can replace undesirable ions in the water supply with other more acceptable ions. For example, commonly used sodium zeolite softener resins replace scale-forming calcium and magnesium ions with sodium ions.

6.2 PRINCIPLES OF ION EXCHANGE

Ion exchange resins are manufactured by several chemical companies, and are widely available from distributors. A reference index of resin types can be supplied by manufacturers. The conventional ion exchange materials used in water conditioning are porous beads having many attached "exchange sites" (Figure 2-10). The resin itself is insoluble in water but is ionizable, thus holding ions of opposite charge at the exchange sites.

FIGURE 1

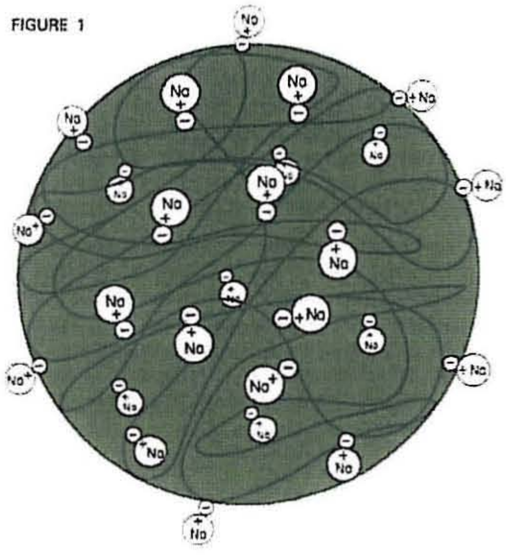


FIGURE 2-10 Model of a cation exchange resin, showing negatively charged exchange sites holding sodium ions

Resins with negatively charged sites are referred to as cation exchange resins since they attract positive ions. Anion exchangers are positively charged and attract negative ions. The porous structure of ion exchange materials permits water to permeate the resin particles, or beads, affording good contact with the exchange sites.

Ion exchange resins have preferences, or "selectivity", for one ion over another. This selectivity depends on ionic charge, size, weight, and solution concentration (See Table 2-6). For example, a cation exchanger holds calcium ions more firmly than sodium ions when immersed in water. For this reason, if a cation exchanger is originally saturated with sodium ions, it can be used to soften water, taking calcium out of the water and releasing sodium in exchange.

Fortunately, the selectivity between these species is reversed at high concentrations so that a strong solution of brine can readily displace calcium from the exchange sites, thus "regenerating" the exchanger by returning sodium ions to their original positions on the exchanger.

TABLE 2-6
Selectivity Of Ion Exchange Resins

↑ Increasing Preference

Cation Exchanger (sulfonic acid type)	Anion Exchanger (quaternary type)
Barium	Iodide
Strontium	Nitrate
Calcium	Bisulfate
Copper	Chloride
Zinc	Bicarbonate
Magnesium	Hydroxide
Titanium	Fluoride
Potassium	Bisilicate
Ammonia	
Sodium	
Hydrogen	

The earliest ion exchange materials were either natural or synthetic zeolites – minerals produced from mixtures of aluminum salts and silicates. When these materials were converted to the sodium form by treatment with brine, they were capable of softening water effectively; however, capacity was low. Research developed plastic materials (resins), which could be converted to ion exchangers by chemical processing.

Many common ion exchange resins are made from two organic molecules – styrene and divinyl benzene. When styrene molecules are treated under proper conditions of temperature and pressure, they form a long chain material called a polymer. Its structure can be made rigid and insoluble by mixing a certain proportion of divinyl benzene with the styrene, forming "crosslinks" between the long styrene polymer chain. This permits the material to grow in three dimensions to form a tight, rigid network.

Reacting these materials in water emulsion forms the plastic into the shape of beads. The finished beads can be converted either to cation exchangers or anion exchangers by suitable chemical reactions. In making a cation exchanger, the bead is treated with a material such as sulfuric acid, which adds an ion exchange site at each hexagonal ring. Anion exchangers are formed by attaching positively charged groups, such as amines, to each hexagonal structure.

6.3 TYPES OF ION EXCHANGE RESIN PROCESSES

The ionizable groups attached to the bead structure determine the functional capability of the resin. Present industrial water treatment resins may be classified as one of four basic types:

- Strong cation, or strong acid (SA)
- Weak cation, or weak acid (WA)
- Strong anion, or strong base (SB)
- Weak anion, or weak base (WB)

6.3.1 Strong Acid Resins

Strong cation, also called strong acid resins, can convert neutral salts into their corresponding acids. This ability, called salt splitting, results in different treated water quality than that obtained by treatment with weak cation or weak acid resins. See chapter 1 for an explanation of strong and weak acids and bases.

Strong cation resins derive their exchange activity from sulfonic acid functional groups (HSO_3^-). When operated on the hydrogen cycle (that is, regenerated with strong acid), they will remove nearly all raw water cations according to these reactions:

$$2RSO_3H + \begin{matrix} Mg^{+2} \\ Ca^{+2} \\ 2Na^{+} \end{matrix} = 2RSO_3\begin{matrix} Mg \\ Ca \\ 2Na \end{matrix} + 2H^{+} \qquad (2\text{-}24)$$

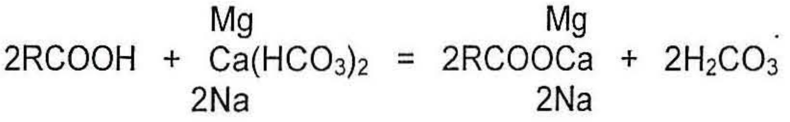
where 'R' represents the resin matrix.

Because these reactions are reversible, when the resin capacity has been exhausted, it can be recovered through regeneration with an acid.

Strong cation exchangers function well at all pH ranges and can split neutral salts into their corresponding acids. These resins have found a wide range of application, being used on the sodium cycle for sodium zeolite softening (see Section 8.0) and on the hydrogen cycle for softening and decationization.

6.3.2 Weak Acid Resins

Weak cation, also called weak acid resins, have carboxylic groups (-COOH) as the exchange sites. When operated in the hydrogen cycle as above, weak acid resins can remove cations associated with alkalinity:



$$2RCOOH + \begin{matrix}Mg\\Ca\\2Na\end{matrix}(HCO_3)_2 = 2RCOO\begin{matrix}Mg\\Ca\\2Na\end{matrix} + 2H_2CO_3 \tag{2-25}$$

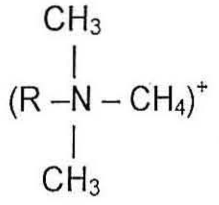
These reactions are also reversible and permit acid regeneration to return the exhausted resin to the hydrogen form.

Because weak cation exchangers do not function efficiently at pH levels below 5.0, they cannot split neutral salts effectively. The main asset of the weak cation resins is their high regeneration efficiency which not only reduces the amount of acid required for regeneration, but also minimizes waste disposal problems.

Weak cation resins are used primarily for softening and dealkalization, frequently in conjunction with a strongly acidic polishing resin.

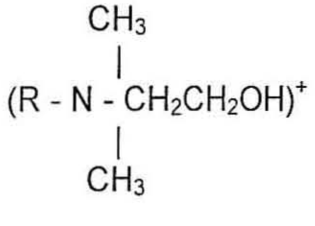
6.3.3 Strong Base Resins

Strong anion, or strong base, ion exchange resins derive their functionality from the quaternary ammonium exchange sites. Two types of quaternary ammonium exchange sites are commercially available and are commonly referred to as Type I and Type II. Type I sites have three methyl groups:



$$\left(R-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N}}-CH_4\right)^+$$

An ethanol group replaces one of the methyl groups in the Type II resin.



$$\left(R-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N}}-CH_2CH_2OH\right)^+$$

The principle difference between the two resins, operationally, is that Type I has a greater chemical stability, and Type II has a slightly greater regeneration efficiency and capacity.

In the hydroxide form, strong base resins will remove all commonly encountered inorganic acids, including silicic acid, according to these reactions:

$$\begin{array}{l} 2H_2SiO_3 \\ 2HCl \\ H_2SO_4 \\ 2H_2CO3 \end{array} + 2ROH = \begin{array}{l} 2HSiO_3 \\ 2Cl \\ 2RSO_4 \\ 2HCO_3 \end{array} + 2H_2O \qquad (2\text{-}26)$$

Like the cation resins reactions, the .anion exchange reactions are also reversible; regeneration with a strong alkali, such as caustic soda, will return the resin to the hydroxide form.

6.3.4 Weak Base Resins

Weak anion, or weak base, resins derive their functionality from primary ($R\text{-}NH_2$), secondary ($R\text{-}NRH^1$) and tertiary ($R\text{-}N\text{-}R_2^1$) amine groups. Weak base resins will exchange strong free mineral acids (hydrochloric, sulfuric and nitric acids). The reactions may be represented as:

$$\begin{array}{l} 2HCl \\ H_2SO_4 \\ 2HNO_3 \end{array} + 2ROH = \begin{array}{l} 2HCl \\ 2RSO_4 \\ 2NO_3 \end{array} + 2H_2O \qquad (2\text{-}27)$$

Weak base resins are essentially mineral acid neutralizers. Because the above reactions are also reversible, weak base resins can be regenerated with caustic soda. Regeneration efficiency of weak base resins is substantially greater than for strong base resins.

While weak base resins readily adsorb free mineral acids, these resins will not remove weakly ionized silicic and carbonic acids. Weak base resins are used in demineralizer systems in conjunction with strong base resins to reduce regenerant costs, to scavenge organics, thereby protecting the more susceptible strongly basic resins, and for service in which carbon dioxide and silica are not important.

Table 2-7 is a condensed summary of advantages and disadvantages of various types of ion exchange resins.

TABLE 2-7

Resin Types Summary

Type of Resin	Advantages	Disadvantages
Matrix Type		
Gel	• High capacity • Lowest price	• Physically weak • Higher potential for fouling
Macroreticular/Macroporous	• Physically strong • Low potential for fouling	• Slight loss of capacity • Slightly higher price
Plastic Type		
Styrene/divinyl benzene (DVB)	• Lowest price	• Higher potential for organic fouling • Plastic is brittle
Acrylic/DVB	• Resists organic fouling • Physically resilient	• Higher price • Thermal limitations
Functional Group		
Strong Acid (SAC)	• Removes all cations • Performance less sensitive to temp or flow rate	• Poorer regenerative efficiency • Low capacity
Weak Acid (WAC)	• Higher capacity • High regenerative efficiency	• Does not remove permanent hardness • Performance sensitive to temp and flow rate
Strong Base/Type 1 (SBA T-1)	• Best silica and CO_2 removal • More stable than Type 2	• Lower capacity • Lower regenerative efficiency • Prone to organic fouling • 120°F max
Strong Base/Type 2 (SBA T-2)	• Slight gain in capacity over Type 1 • Slight gain in regenerative efficiency	• Poorer chemical and physical stability • 105°F max
Weak Base	• Moderate capacity • Good regenerative efficiency	• No silica or CO_2 removal • Poorer chemical and physical stability

6.4 ION EXCHANGE RESIN CHARACTERISTICS

There are key characteristics of resins that are important. An understanding of these properties will help in selecting, maintaining and troubleshooting ion exchange materials.

Many things affect the performance of an ion exchange system. Each of these factors falls into one of the following categories:

- Feedwater quality
- System design
- System operation
- Resin Characteristics
- Resin quality

The quality of the water, and system design and operation, are extremely important and are discussed throughout this manual. The last two items (resin characteristics and quality) relate specifically to ion exchange resins and are discussed below.

6.4.1 Resin Type and Structure

As discussed, cation resins fall into two general categories: strong acid and weak acid. Strong acid resins can remove all types of cations. Weak acid resins can only remove certain types of cations; but they operate at higher regeneration efficiency than strong acid resins.

Similarly, most anion resins are either strong base or weak base. Strong base resins can remove all types of anions, while weak base resins cannot. But weak base resins offer greater efficiency.

Strong base resins are further classified as Type I or Type II, as explained in section 6.3.3. The Type II resins are more efficient; but they lose salt splitting characteristics at lower temperatures than Type I resins. Type I resins, in addition to greater thermal stability, also provide better silica removal.

Most ion exchange resins have either a gel or a macroporous structure. Gel resins are transparent beads with a low percentage of divinyl benzene "crosslinkage" in the polymer. Macroporous resins are opaque beads with a higher percentage of divinyl benzene crosslinkage and a number of discrete pores; hence, the name "macroporous". Each structure has certain advantages and disadvantages.

6.4.2 Ion Exchange Capacity

Ion exchange capacity relates to the number of ions that can be exchanged per unit of resin volume. If resin capacity is less than expected, run times will be shorter and more regenerant chemicals will be consumed.

The actual operating capacity of any resin depends on many site-specific factors as well as resin type, including influent water composition, effluent water quality, regenerant dosage, and flow characteristics.

Gel-type resins usually provide 20 – 30% more capacity than macroporous resins.

6.4.3 Kinetics

Kinetics refers to the speed of reaction, in this case between the ions in the water and the ion exchange resin. The ion exchange process takes place not only on the surface of the bead but also inside the bead. Therefore, the solution has to be able to diffuse through the resin structure to find the exchange sites within the bead. As a result, the tighter the resin structure, the more difficult the diffusion and the poorer the kinetics.

Resins can range from 2 to 20% crosslinkage. Low crosslinking creates beads that break easily. Too much crosslinking leads to rigid resins and poor kinetics. A compromise is 8% crosslinking, which is most common for strong acid cation resins used in softeners and demineralizers. Some manufacturers offer a 10% crosslinked gel cation resin.

In order to take advantage of the strength of higher crosslinked resins without losing too much on kinetics, macroporous resins were developed. Macroporous cation exchange resins are commonly available in 12% and 20% crosslinkage. A slight drawback for macroporous resins is a slightly lower exchange capacity.

6.5 PHYSICAL PROPERTIES OF RESINS

6.5.1 Particle Size

The particle size distribution of the resin will have a significant effect on ion exchange performance. The smallest resin beads tend to be washed away during the initial backwash, so their ion exchange capacity is not utilized. Other small beads fill up voids in the bed and increase pressure drop. Large beads have longer diffusion paths than small beads, so their capacity is not well utilized, especially at higher flow rates.

The size distribution also affects hydraulic performance – including pressure drop, degree of bed expansion, and the filtration function in condensate polishing. Size distribution should not vary widely and should be specified.

6.5.2 Classified Density

Ion exchange resins are purchased by volume and shipped in a specific ionic form, i.e., sodium or hydrogen form for cation resin and chloride or hydroxide form for anion resin. The classified density determines how many pounds of resin must be loaded into a resin vessel to obtain the designed volume in the backwashed, settled and drained condition.

6.5.3 Water Retention Capacity

Many of the chemical and physical properties of an ion exchange resin are determined by its "crosslinkage", i.e., the percent of divinyl benzene (DVB) in the resin. Small variations in crosslinkage can affect ion exchange capacity, selectivity, physical stability, oxidation resistance and other properties.

Water retention capacity is an inverse indicator of crosslinkage. Less crosslinkage allows higher water content. Water retention capacity can be easily checked. The amount of water in a resin bead also affects its density. Variations in water retention capacity can change a resin's hydraulic properties, particularly the degree of bed expansion.

6.5.4 Physical Stability

Resin bead breaks up into smaller particles known as fines. These fines will be lost during backwash, lowering overall bed capacity. Others will fill up voids and increase the pressure drop across the bed.

In mixed beds, cation fines are nearly certain to end up with the lower density anion resin for regeneration, contributing significantly to capacity loss and water quality problems caused by cross contamination.

Fines can also fill up voids in one part of a packed resin bed and force the water to flow only through other parts of the bed. This "channeling" of flow prevents part of the bed from being used, which will reduce bed capacity and cause an increase in regenerant use, since the bed will have to be regenerated more frequently.

Bead strength is measured by a crush test and other tests called sphericity before and after attrition.

Osmotic shock is due to the sudden contact of the resin with a solution of much higher concentration. A sudden dewatering of resin occurs and the resin shrinks. Immediately after, the solution penetrates the resin and sudden swelling occurs, hence, some beads may break.

Mechanical attrition is due to mechanical pressure of the resin. This is often due to high pressure drops across the resin bed.

Particle fragmentation results in loss of resin, increase in pressure drop and channeling.

Macroporous resins do not swell and shrink as much due to higher crosslinkage and can be more resistant to osmotic shock.

6.5.5 Thermal Stability

When exposed to warmer waters (120°F or higher for Type I; 95°F or higher for Type II) the exchange sites will degrade. Most common degradation is the conversion of the strong base site to a weak base site. Type II strong base anion resins are more subject to such degradation due to their chemical structure. Therefore, as a strong base anion resin ages, a larger and larger amount of strong base sites will be converted to weak base sites. Since only strong base sites are able to exchange weak acids such as silica or carbon dioxide, there comes a point where the strong base anion resin has such a low salt splitting capacity that it is no longer able to remove sufficient silica or CO_2 from the water, at which time it has to be replaced.

6.5.6 Chemical Stability

DVB is subject to oxidation. For strong acid cation resins, oxidation is due mostly to oxygen (present in surface waters) and free chlorine (when the water is chlorinated). Oxygen is not a serious problem in cold water, but when water is heated, dissolved oxygen becomes more aggressive.

Free chlorine is a lot more aggressive than oxygen (even in heated water) and should be reduced to less than 0.1 ppm. This is often done with sodium sulfite.

The result of resin oxidation is decrosslinking, leading to loss of physical strength and stability. Decrosslinking has the following effects:

- Cation resins:
    - Loss of matrix physical strength
    - Increase in water retention capacity
    - Increase in volume
    - Decrease in wet volume exchange capacity
    - Decrease in density
    - Decrease in bead strength
- Anion resins:
    - Strong base anion resins degrade to weak base sites, causing a decrease in operating capacity.
    - Weak base anion resins degrade weak base exchange sites into weak acid exchange sites, resulting in a decrease in capacity and increase in rinse water requirement.

6.5.7 Regeneration Efficiency

Capacity and kinetics describe the ability of a resin to remove unwanted ions from water. Regeneration efficiency concerns performance during regeneration. Higher regeneration efficiency can lower operating costs significantly.

Weak acid cation resins are more efficient than strong acid cation resins. Anion resins can generally be ranked from best to worst regeneration efficiency as follows: (1) weak base, (2) intermediate base, (3) strong base, Type II, (4) strong base, Type I.

In general, the same structural effects that allow high capacity and good kinetics lead to greater regeneration efficiency. The low-cross-linked gel resins tend to have an advantage over the higher-crosslinked macroporous resins.

6.5.8 Organic Fouling Resistance

Another problem for ion exchange performance, particularly where feedwater is drawn from lakes and rivers, is organic-bearing water. Organics can be a problem because the large organic molecules tend to become trapped inside the pores of an ion exchange resin and cannot be removed by normal regeneration procedures.

If organics cannot be totally removed upstream, resins should be used that tolerate and even remove organic material. Since most organics form negative ions, fouling is primarily a threat to the anion resins, particularly the first one in the demineralizer train.

Some resins use acrylic backbones instead of polystyrene for certain resins. These resins are gaining in popularity. They have a higher strength, higher operating capacity and are less prone to organic fouling.

6.6 INSPECTING ION EXCHANGE EQUIPMENT

Water treatment personnel normally do not supply chemicals for use in ion exchange pretreatment systems, except for cleaners and similar products. Therefore, suppliers may ignore the pretreatment train or declare that it is not their responsibility. This may be technically correct. However, water treatment personnel should consider the pretreatment train as part of the total system and encourage facility personnel to maintain their equipment. There is often a direct relationship between the pretreatment system and internal boiler water treatment. If the boiler feedwater does not meet required quality, it may be impossible to make the internal boiler water treatment program work as required (see chapter 3). Serious boiler failures, and at least one fatal accident, have been traced to poor feedwater quality and to failure of both the boiler operators and the water treatment supplier to correct obvious problems in the pretreatment train.

6.6.1 Mechanical Inspection Checklist

Ion exchange systems require regular inspection and mechanical maintenance to help ensure long, trouble-free runs. While mechanical inspections are the responsibility of the facility operations staff, water treatment personnel can play an important role by encouraging maintenance personnel to do this work. The mechanical information in this section will help water treatment personnel to understand the complexities of mechanical inspections and talk knowledgeably with facility staff.

Vessel inspections should be done both as routine maintenance and to troubleshoot problems. Inspect the unit at end of the service cycle, before backwashing. The top of the resin bed will be at its dirtiest and evidence of service cycle channeling will not have been erased by the backwash.

Section 2.01 Following is a list of items that should be covered in a mechanical inspection, and that may cause system operational problems:

- Condition of vessel
- Leaks in pipes, joint flanges
- Pluggage of lines

- Inoperative valves and flow meters
- Metal, plastic or rubber lining condition
- Splash plates condition
- Condition of laterals – intact, bent, cracked, missing, orientation of holes
- Lateral screening
- Regenerant distributor condition

6.6.2 Resin Bed Inspections

When a resin vessel is opened for inspection, the first thing to examine is the condition of the top of the resin bed. Following are important checkpoints:

- Resin bed condition – the beads should be the shape, size and color of new resin. See section 6.7 on resin analyses for more on this subject.
- Deposits on bed – the bed should be clean.
- Shape of top of resin bed:
    - Level to ± 1 inch = OK.
    - Even, but sloped to one side (clogged upper and/or lower distributors).
    - Depressed in center (broken or missing splash plate, low service flow).
    - Depressed around outer edge (flow rate too high for distributor design, missing lateral end caps, fouled bed).
    - Random cratering (clogged or damaged upper and/or lower distributors, fouled bed).
    - Patterns of ridges and valleys corresponding to splash plate shape (poorly designed splash plate, often seen in homemade units).
- Height from top of resin bed to regenerant distributor (too much rim can cause poor regeneration and service flows and cause channeling, too little can cause lower capacities)

6.6.3 Operational Checks During Vessel Inspection

As part of regular ion exchange vessel inspections, operation of the water distributor lines should be observed:

- Service Distributor: Observe spray pattern over normal operating range. If possible, check uniformity of flow. A plugged distributor will show an uneven spray pattern.

- Regenerant Distributor: Observe spray pattern with only diluted water at the normal regeneration flow rate (slow rinse step). Block out and tag regenerant valve. Check uniformity as for service distributor.

- Backwash Distributor: Completely drain the bed. With a view of the entire bed surface initiate a backwash at the currently used flow setting.

6.7 RESIN SAMPLING AND ANALYSIS INTERPRETATION

Water treatment suppliers may be asked, or may offer, to do resin inspections and analyses as part of their service program, and to help maintain boiler feedwater quality.

Annual resin sampling is normally adequate unless significant deterioration in unit performance is observed. Sampling should take place at the end of the service cycle, before backwashing and after the unit has been inspected. Some water should be present in the bed to help the insertion of a core sampler. The sample should be a composite of several random samplings across the resin bed. Be sure to get a good core sample – not just the top of the bed.

6.7.1 Resin Analyses

Resin analyses must be performed in qualified laboratories. Most resin manufacturers provide this service, as do many commercial laboratories.

See Tables 2-8 and 2-9 for interpretation of resin analyses. Resin analyses include microscopic, physical and metal analyses. Table 2-10 indicates normal ranges for resin moisture, density, salt-splitting and total capacities.

TABLE 2-8
Interpretation Of Resin Analyses

Item	Test Result	Comments
Microscopic Analysis		
Color		Due to batch variations, color can be misleading. Abnormal color may indicate foulants.
Crazing		The abundance of microcracks in a gel bead is termed crazing. It can be due to thermal or osmotic shock.
Physical Analysis		
Broken beads	<5%	OK.
	>5%	Fines should be removed and resin replaced. If unit is showing high-pressure drop, high broken beads may be to blame.
	>15%	Resin degradation possible.
Coating	Light to heavy	Light coating is usually no problem; except for oil.
Moisture (See below)	Gel strong acid cation	Most useful test result for integrity of this resin.
		Beginning decrosslinking; check 6-12 months later.
	Low 50's	
		Continuing decrosslinking, possible re-bed.
	High 50's	Extensive decrosslinking, probably re-bed if problem with pressure drop or service channeling.
	60's	
Friability		Possible loss of crosslinking.

TABLE 2-9
Inorganic Analysis-Metals

Test Result	Comments
<50 gms/ft^3	Irrelevant except for strong base resins: Iron usually accompanies organic fouling
50-200 gms/ft^3	Usually not a problem except: • Iron >150 on Strong Acid Cation can decrease runs • Calcium/magnesium on strong base anion can leak hardness
Iron	From influent water or poor quality regenerant
Aluminum	Strong Acid cation: Alum based floc carryover
Calcium	Strong Acid cation: Calcium sulfate from improper acid regeneration
Silica	Strong Acid cation: Sediment in influent water
Magnesium	Strong and weak acid cation: Magnesium hydroxides, precipitating softener upset
	Strong base anion: Leakage from cation, contaminated caustic

TABLE 2-10
Summary of Resin Moisture, Density and Capacity Data

Characteristic	Units	Weak Acid Cation		Strong Acid Cation		Weak Base Anion		Strong Base Anion	
		Gel	Macro	Gel	Macro	Gel	Macro	Gel	Macro
Moisture	Percent	42-46	46-50	44-48	46-50	60-68	55-60	40-50	55-60
Density	lb/cu. ft.	46-48	40-42	50-54	48-50	42-46	36-40	42-45	40-44
Salt splitting capacity	kilograins /cu. ft.							20-25	16-20
Total capacity	kilograins /cu. ft.	85-88	75-78	41-46	37-39	33-35	24-26	25-31	20-25

6.7.2 Total Organic Carbon (TOC) In Regenerant Effluent

It is good practice to obtain an indication of the level of adsorbed organic matter in the resin beads by measuring the amount of organic carbon released from the beads on heating. There is a general correlation between the test results and the occurrence of organic fouling. 100 – 200 ppm TOC is medium fouling. >200 is heavy fouling, indicating the bed should be cleaned.

6.8 CLEANING ION EXCHANGE UNITS

Resin cleaning is an important service that water treatment suppliers can provide for their customers. Some cleaning may be done routinely, particularly for iron removal, while more specialized cleaning will be done as required, based on results of resin analyses.

Fouling of resins can significantly affect performance of ion exchange systems. Contamination can occur, most commonly, as a result of contaminants in the make-up water, as well as poor regenerant quality and operations. Use of off-spec caustic is a classic example of regenerant-caused fouling. Calcium sulfate fouling is normally due to high concentrations of sulfuric acid being used during regeneration. A pro-active program of resin sampling and analysis and cleaning when needed can provide significant payback.

6.8.1 Routine Maintenance

Many waters which have been zeolite softened (section 7) contain significant amounts of iron which cannot be removed from the active resin sites by normal brine regeneration techniques. To maintain these resins at peak operating efficiency, resin cleaners are added to the brine tank at the rate of 1 – 2 quarts per cubic feet of resin in the softener. The unit is then regenerated in the normal manner. The frequency of use and the dosage level depend upon the severity of the fouling problem.

6.8.2 Cleaning Severely Fouled Resin Beds

The cleaning of severely fouled resin must be done off line. Prior to cleaning, backwash the resin in the normal manner to remove dirt and particulates in the resin bed. After backwashing, drain the bed and open the hand hole at the top. Add an appropriate amount of resin cleaner, and then refill with water until the resin bed is just covered. Then, insert an air lance through the hand hole into the resin bed. It is recommended that the air lance be an open pipe with a bar welded across the top of it to prevent insertion below the resin into the support bed. Upsetting the support bed could result in severe resin loss and the need to rebuild the unit.

Once the air lance is inserted, turn on the compressed air and regulate it to achieve mild agitation in the bed. In a larger unit, it will be necessary to move the lance every 30 minutes or so to ensure that the entire bed is covered. It will normally take from two to four hours to thoroughly clean the resin bed.

After agitation, remove the air lance and close the hand hole. Refill the softener and backwash manually until the backwash water runs clear. Then, regenerate the unit twice prior to return to service.

6.8.3 Inorganic Resin Contaminants

The following sections describe some of the most common inorganic contaminants found on ion exchange beds, and general methods for removing these contaminants:

- Iron: Ferric iron may be present in the raw water, or it may be carried over from clarification processes. Iron can coat cation resins and block exchange sites. Cleaners based on acid plus hydrosulfite or other reducing agents are best for cleaning cation resins. However, organically bound iron will pass through the acid cation resin in a demineralizer train and foul the anion resin. For cleaning anion resins, warm brine + caustic, or sodium hypochlorite, will restore part of the lost capacity, but full recovery is usually not attained. If iron fouling continues to be a severe problem, pretreatment to remove iron is usually required. This may involve improvement of clarification processes or special treatment with potassium permanganate.
- Manganese, present in some well water supplies, causes capacity loss in much the same manner as iron.
- Aluminum fouling is usually the result of aluminum hydroxide carried over from the clarifiers or precipitation softeners. Aluminum floc, if carried through the filters, will coat the resins. Aluminum on cation resins operating in the sodium cycle may be removed by either acid or caustic cleaning because aluminum is amphoteric (chapter 1). Aluminum is usually not a problem in demineralizers because removal occurs during acid/caustic regeneration. The best solution to aluminum fouling is to correct clarifier carryover problems, adding post-clarifier filtration if necessary.
- Hardness may carry through filters associated with precipitation softeners. Also, precipitation can occur in ion exchange resins following cold lime softeners. At ambient temperatures, precipitation reactions may not be complete in the softeners, so that further precipitation may occur in downstream equipment. An acidic cleaning chemical can dissolve hardness precipitation on the resins. Increasing residence time in the softeners will usually correct this problem.
- Calcium sulfate precipitation may occur in cation exchangers operating in the hydrogen cycle. Sulfuric acid is the usual regenerant. If introduced at too high a concentration, or if the regenerant flow rate is too low, calcium sulfate will precipitate. Cation resins severely fouled with calcium sulfate are usually discarded.
- Silica: Polymerization of silica may occur in anion resin beds. At the start of a regeneration, silica is eluted in quantity. At exhaustion, the water in the anion unit is acidic. If flow rates are not correct, polymerization may occur in strong base units. In a two-bed weak and strong anion system, use of all the waste regenerant from the strong base unit for regenerating the weak base resin will likely cause silica polymerization in the weak base unit. This can be avoided by wasting the first 20 to 25 percent of the regenerant from the strong base unit. Alternately, the weak base resin may be neutralized and partially regenerated by applying about one-half the weak

base regenerant requirement as fresh caustic. In most cases, warm (120°F) regeneration with fresh caustic will remove polymerized silica.

6.8.4 Organic Contamination

Surface waters may contain hundreds of parts per million of natural and man-made synthetic organic matter. Natural organics are derived from decaying vegetation and are aromatic and acidic in nature, frequently complexed with a heavy metal such as iron. Synthetic organic matter includes detergents and other chemicals that seep into natural water supplies.

Organic fouling occurs primarily on strong base anion resins and is often irreversible. The effect of organics on anion resins is the degradation of the strong base sites (reduction of salt splitting capacity). The functionality will change from strong base to weak base. Thus, a fouled resin may exhibit a good total exchange capacity but very poor salt splitting capacity. Loss of salt splitting capacity will be reflected in reduced ability to remove carbonic and silicic acids.

Organic fouling of anion resins is reflected by a tea to dark brown colored wastewater during caustic addition and rinse. Operationally, the anion exchange effluent will show higher conductivity and lower pH water than should be produced by uncontaminated resin.

The following methods can be used to reduce organic matter in the feed water to an ion exchange train.

- Pre – and post-chlorination at the clarifier to oxidize organic compounds, followed by clarification and filtration.
- Activated carbon filtration.
- Macroporous resins (weak base) ahead of the strong anion resin will adsorb organics. These are sometimes called organic trap resins.
- Acrylic resins have better resistance to organic fouling than other types, and have good strong base capacity.

Cleaning procedures to remove organic foulants from anion resins include:

- Alternate warm salt and caustic (120°F)
- Hydrochloric acid alone or in place of salt
- Solutions of 0.25 to 0.5 percent sodium hypochlorite

These procedures may remove much of the organic contamination from strong base anion resins, but recovery of salt splitting capacity is usually not successful.

7.0 Sodium Zeolite Softening

7.1 INTRODUCTION

Sodium zeolite softening is an ion exchange method for removing hardness from water supplies by exchanging calcium and magnesium ions for sodium. The name "zeolite" derives from natural silicate-based materials (zeolites) that can perform this ion exchange function, The name is now applied both to the softening process and to the synthetic organic resins now used for softening water (see section 6 for basic ion exchange information).

Zeolite softening is widely used for domestic, commercial, and industrial water preparation. Zeolite softening has several important advantages over precipitation softening (section 4):

- No solid sludge is generated.
- No need to handle lime.
- Much smaller space requirement. Zeolite units range in size from home units to industrial systems generating thousands of gallons per minute of softened water.

7.2 PRINCIPLES OF ION EXCHANGE SOFTENING

In sodium zeolite softening, water containing calcium and magnesium hardness is passed through cation exchange resin beds having sodium as the exchangeable ion. In equation 2-28 below, the ion exchange material is expressed as RNa, where R stands for the resin matrix and Na is its mobile exchange ion. The hard water exchanges calcium and magnesium ions rapidly, so that water in the effluent will be almost completely softened. Calcium and magnesium salts are converted into corresponding sodium salts.

$$2RNa \quad + \quad \overset{Mg^{+2}}{Ca^{+2}} \quad = \quad R_2\overset{Mg}{Ca} \quad + \quad 2Na^{+} \qquad (2\text{-}28)$$

The reaction proceeds toward the right to its completion; that is, until the bed becomes completely exhausted or saturated with Ca and Mg ions. In order to reverse the equilibrium so that the reaction proceeds toward the left, the concentration of sodium ions has to be increased. This increase in sodium ions is accomplished by using a brine solution of sufficient strength that the total sodium ions present in the brine are significantly more than the total equivalent of Ca and Mg in the exhausted bed. This reverse reaction is carried out in order to bring the exhausted resin bed back to its sodium form. This process is known as "regeneration".

7.3 ZEOLITE SOFTENING OPERATIONS

7.3.1 Softening

When a softener with fresh resin is put into service, the sodium ions in the surface layer of the bed are immediately exchanged with calcium and magnesium, thereby producing soft water with very little residual hardness in the effluent. As the process continues, the resin bed keeps exchanging its sodium ions with calcium and magnesium ions until the hardness concentration in the effluent increases rapidly. This is called the "breakthrough point", at which the softening run is ended.

Table 2-11 shows typical performance data for an industrial zeolite softening unit.

TABLE 2-11
Zeolite Softening Performance

Item	Influent, mg/L	Effluent, mg/L
Hardness, ppm as $CaCO_3$	50	0.1
Hardness, ppm	500	1.0
Hardness, ppm	1,000	2.0
pH	7.5	7.5 ± 0.3
Turbidity, JTU	2 – 5 (max.)	<1

The softening process can theoretically be extended to a point where hardness levels entering and leaving are the same, and the bed is completely exhausted. In practice, the softening is never extended to reach this stage. The process is ended at some predetermined effluent hardness, much lower than the influent hardness, usually <1 ppm. After the resin bed has reached this point, the resin bed is regenerated with a brine solution.

7.3.2 Regeneration

Regeneration of the resin bed is never 100% complete. Some traces of calcium and magnesium remain in the bed and are present in the lower bed level. In the service run, sodium ions exchanged from the top layers of the bed form a very dilute regenerant solution, which passes through the resin bed to the lower portion of the bed. This solution tends to leach some of the hardness ions not removed by previous regeneration. These hardness ions appear in the effluent water as "leakage". Hardness leakage is also dependent upon the raw water characteristics. If the Na/Ca ratio and calcium hardness is very high in the raw water, leakage of hardness ions will be higher.

7.3.3 Operations

Following are the basic steps involved in normal operation and regeneration of a zeolite water softener:

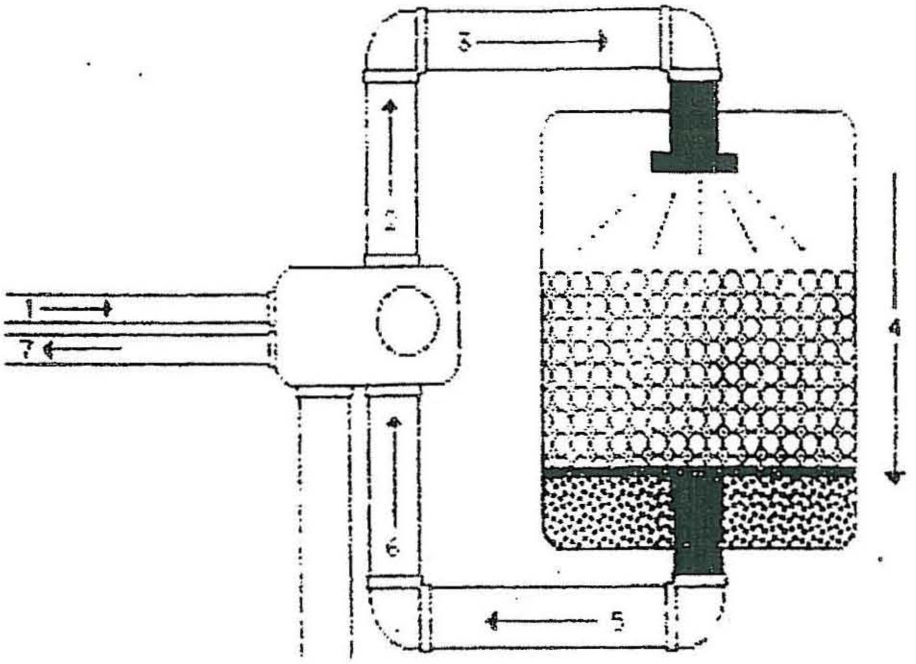


Figure 2-11: Normal operation of a sodium zeolite softener.

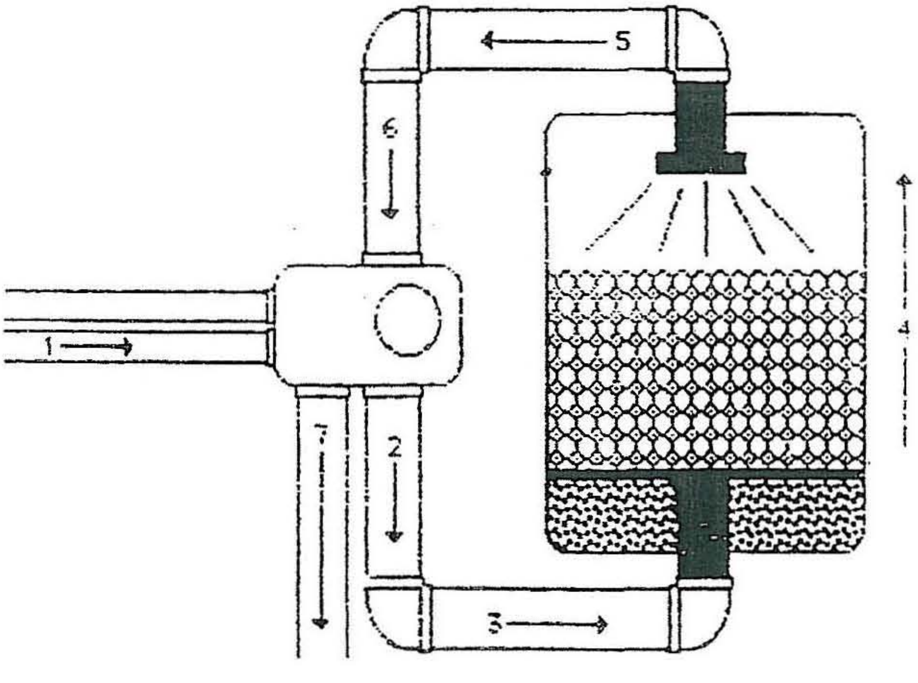


Figure 2-12: Backwash operation of a sodium zeolite softener.

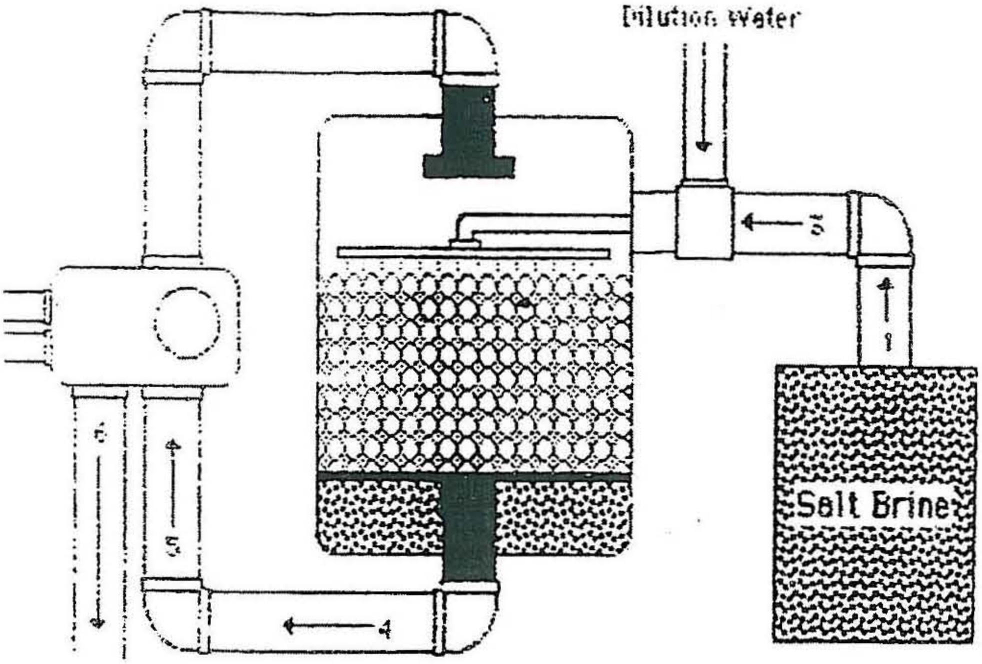


Figure 2-13: Regeneration of a resin bed.

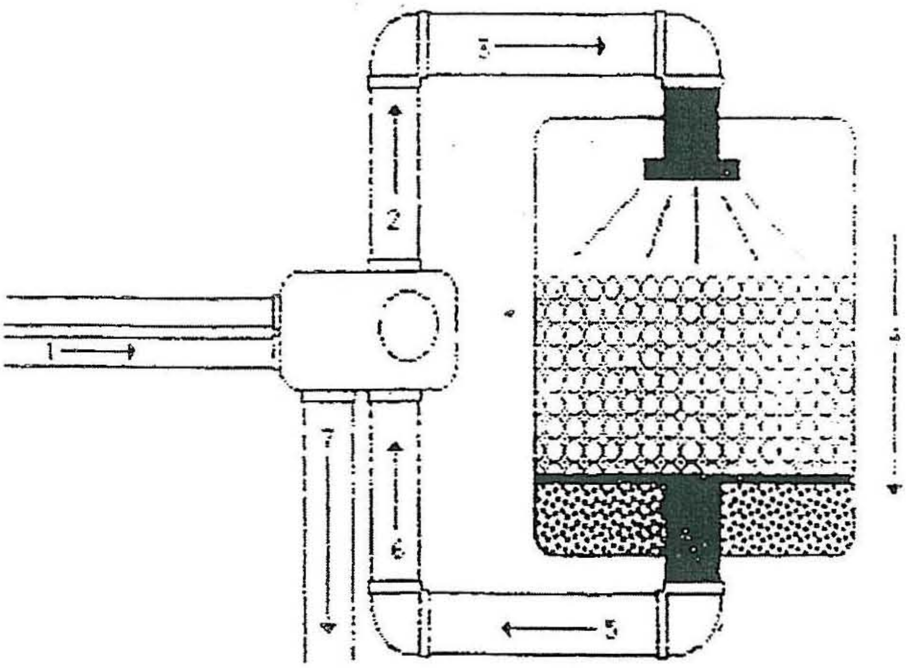


Figure 2-14: Resin bed rinse operation.

- Service (see Figure 2-11): For service, water enters the softener in step (1) through an inlet valve, usually through a multiport valve. The water in the valve (2) enters the softener from the top (3). The water is distributed through the resin bed (4) where the ion exchange occurs. The softened water passes through a series of strainers and is collected in the bottom of the softener (S) where it is returned to the multiport valve (6). The softened water passes through the valve and is diverted to the process supply line (7). Some softeners use individual inlet and outlet valves for each step, instead of the common multiport valve illustrated here. Some valves are manually operated and some are operated automatically; however, the basic principles are the same in all softeners.

- Backwashing (see Figure 2-12): The backwash step is performed immediately after the softener is removed from service. Clean water is diverted through the multiport valve and forced upward through the bed and out the top of the softener to the drain. This procedure expands and redistributes the resin bed prior to regeneration. It also removes dirt, debris, and broken beads from the softener and reduces resin fouling. Backwashing is normally carried out at 5-6 GPM/ft^2. However, the backwash flow rates are proportional to the temperature of the water. It is always a good practice to inspect the backwash effluent periodically for resin, which might be entrained if flow rates are excessive.
- Brine Injection or Regeneration (See Figure 2-13): After backwashing, a 5-10 percent brine solution is injected during a 30 minute period. The maximum exchange capacity of the resin is restored with a 10 percent brine solution. The brine is injected through a separate distributor placed slightly above the resin bed.

  This is the most critical step, since the brine strength, flowrate, and distribution of the brine all relate directly to softener performance. The brine regeneration restores the exchange capacity of the resin beads by displacing the calcium and magnesium ions that have collected on the beads with sodium ions from the brine solution. The brine saturator and the brine day tanks should be cleaned periodically to keep debris from entering the ion exchange softener vessel during regeneration.
- Displacement or Slow Rinse (see Figure 2-14): After brining, the salt solution remaining inside the vessel is displaced slowly, at the same rate as the brine injection rate. The slow rinse volume should not be less than 10-gallons/cu. ft. of the resin. The actual duration of slow rinse should be based on the specifications of the manufacturer of the equipment and resin type.
- Fast Rinse: Rinsing is continued to remove excessive brine from the resin. The rinsing operation is generally stopped when the effluent chloride concentration is less than 5 – 10 ppm in excess of the influent chloride concentration and the hardness is equal to or less than 1 ppm as $CaCO_3$. Following fast rinse, the unit is returned to service.

7.3.4 Control Tests

Table 2-12 lists the chemical tests used to control zeolite softener operations.

TABLE 2-12

Ion Exchange Softener Control Tests

Test	Purpose	Results	Comments
Soluble Hardness			
Influent	Check hardness coming into unit.	(depends on water)	Compare test results to design value; will affect throughput.
Effluent	Check leakage and exhaustion of unit.	0.2 – 0.5 ppm <0.2 >1 >2 - 5	Acceptable performance. Good leakage. High leakage. Unit exhausted.
Acid Hardness			
Influent	Check particulate carryover from precipitating softener or filter carrythrough.	1 – 2 ppm <2 >5	Acceptable performance. Check pretreatment. Carryover or carrythrough needs immediate attention.
Effluent	Check particulate carrythrough.	0 ppm >0.5	Expected results. Hardness carrythrough.
Turbidity	Tests particulate loading and filter performance.	2 – 5 JTU <2 >5	Acceptable. Very good filtration. High particulate loading on resin unit.

7.4 TROUBLESHOOTING

Common problems encountered with an ion exchange softening system are (1) high hardness in effluent, (2) low throughput volume, (3) extended rinse time, and (4) loss of resin. The first three problems are usually related to any or all of the following causes:

1. Improper regeneration procedures.
2. Poor regeneration because of faulty brine distribution and/or underdrain collection system.
3. Resin fouling with calcium, iron, and aluminum.
4. Organic matter and calcium sulfate deposition caused by the rock salt used for regeneration.
5. Physical breakdown of resin beads into fines, causing channeling.

A troubleshooting guide for sodium zeolite softeners is shown in Table 2-13.

TABLE 2-13

Zeolite Softener Troubleshooting Guide

Problem	Possible Causes	Check	Action to Correct
Short Runs			
Continual short runs, slow appearance of problem in operating history.	Change in raw water hardness	Influent hardness.	Consider softer source or higher regeneration level.
	Poor regeneration	Check regeneration review. Elution study (see section 7.5)	Readjust flows and/or brine strengths based on review and elution study.
	Channeling due to bed fouling or distributor problem	Influent turbidity history. Bed inspection precipitation of soluble iron.	Improve performance of equipment ahead of softener. Check backwash. Replace/repair distributor or strainer.
	Resin fouling	Resin analysis	Reduce source of foulant. Clean resin.
	Loss of resin	Excessive backwash flow rate. Collector strainers problem Check for subfill in resin.	Readjust flow rate. Fix strainers Repair distributor element. Replace subfill contaminated with resin.
High Hardness			
	Raw water by-passing unit	Test hardness before and after valve.	Repair or replace valve.
	Resin fouling.	Measure Ca/Mg ratio before and after unit.	Different ratio before and after may indicate resin fouling. Check pretreatment.
	Deteriorating regeneration practice	Revise Procedure.	Elution study.
	Increased raw hardness	Change in raw water hardness.	Review regen procedure
	Previous complete hardness breakthrough	Check history.	Double regeneration.

High Pressure Drop	Bed fouling	Channeling.	Readjust flow for current backwash water temperature.
	Poor backwash	Review backwash rate.	Adjust rate
	Plugged under-drain strainers	Check unit.	Repair and/or clean
	Deteriorating Resin	Moisture content of bead, fines.	Replace resin when needed.
	Valve blockage	Pressure drop through bed history.	Check and replace valve.
		Have plant interchange gauges with another unit.	Replace if necessary.

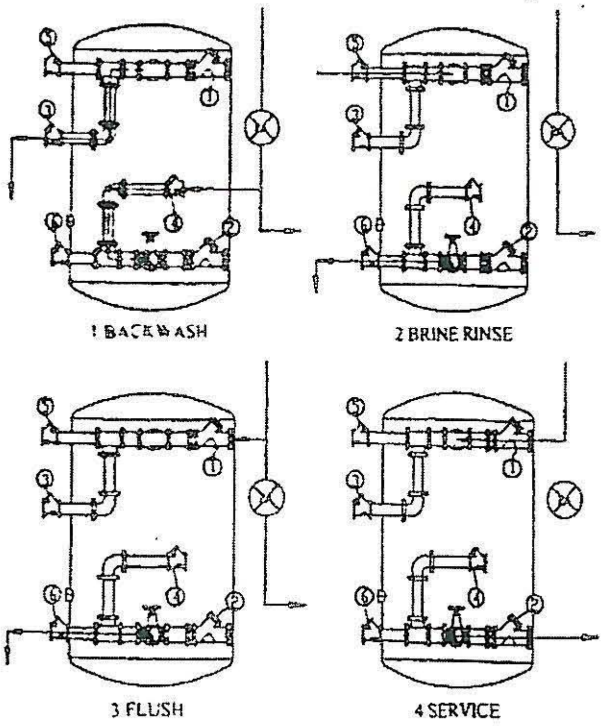
7.5 BRINE ELUTION STUDIES

Problems in zeolite softener systems are often due to poor regeneration practices. A brine elution study is a common technique used to troubleshoot this process. The study plots the concentration (specific gravity) of brine from a zeolite softener during a regeneration, using a hydrometer and graduated cylinder. Cycle times are also recorded.

Given the capacity of any resin with a given brine concentration used as regenerant (data available from resin manufacturers), the system's expected performance can be compared with actual results.

As covered briefly above, following is a typical regeneration sequence. Sample the effluent and measure specific gravity as the unit proceeds through a regeneration cycle.

- Counterflow backwash the resin. Specified rates are based on temperature and manufacturer's data. Backwashing removes surface deposits and fines, classifies resin, and conditions the resin bed for proper regeneration.
- Regenerate: Brine regeneration consists of educting saturated brine from a brine tank or other source and diluting it to generally 8 to 10% by weight NaCl. The brine should elute through the resin bed, first increasing in concentration, then reaching a peak and decreasing until only dilution water is present.
- Rinse: The fast rinse cycle rinses the final residual brine from the resin bed. The regeneration cycle is complete when the unit returns to service or stand-by position.



Cycle	Position	Valves Open
Backwash	#1	2a, 3, 4
Brine & Rinse	#2	2a, 5, 6
Fast Rinse	#3	2a, 1, 6
Service	#4	1, 2

Valve 2a is an optional by-pass valve to supply hard water during regeneration on single units.

Figure 2-15: Regeneration Cycles

Figure 2-15 shows water flow during regeneration cycles. A typical valve arrangement depicts the flow direction for each cycle. In order to perform the brine elution study, it must be possible to gather samples at the effluent of the softener. Table 2-14 shows brine density (specific gravity) and pounds of NaCl per gallon.

TABLE 2-14

Specific gravity and pounds of salt per gallon for brine solutions of various concentrations.

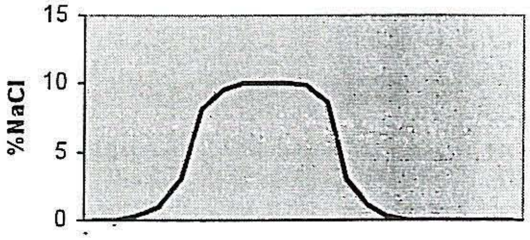
% NaCl	Section 2.02 Specific Gravity	Section 2.03 Lb. NaCl/gal
4	1.029	0.347
6	1.040	0.535
8	1.059	0.724
9	1.067	0.825
10	1.074	0.925
12	1.089	1.136
13	1.096	1.278
14	1.104	1.390
15	1.112	1.470
16	1.119	1.586
18	1.135	1.834
20	1.151	2.082
23	1.176	2.504
26	1.201	2.926

Samples should be taken every 5 minutes over the entire brine and slow rinse cycle. Once the elution data are plotted, the shape of the curve provides an indication of the regeneration result and information on the cause of the operating problems. Figure 2-16 shows typical elution curves, possible problems and corrective actions.

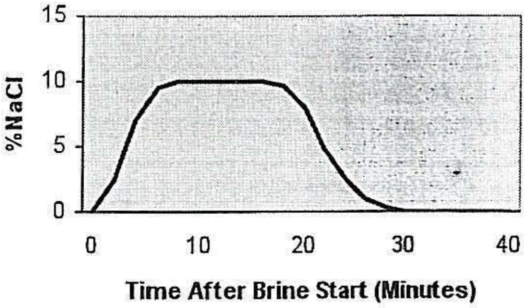
Figures 2-16, a-g. Brine elution curves

Issue | **Elution Profile** | **Problem and Causes**

A. Normal regeneration

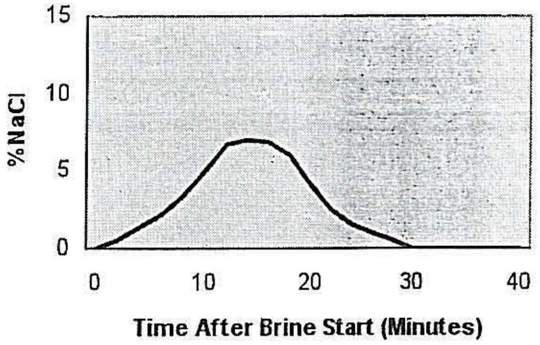


B. Regenerant channeling



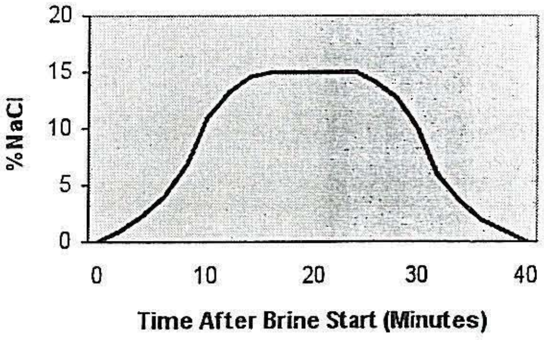
Short runs,
Hardness leakage
Causes:
-Broken distributors
-Plugged strainers
-Poor backwash

C. Low salt concentration



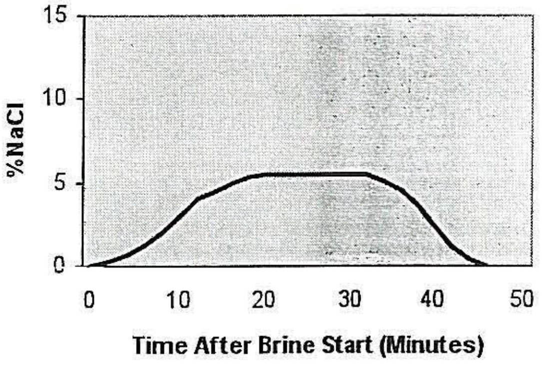
Short runs
Causes:
-Plugged brine system or
eductor too small
-Dilution flow wrong

D. Salt concentration too high



High salt use
Causes:
Brine step timer
setting too high

E. Excessive time, low brine



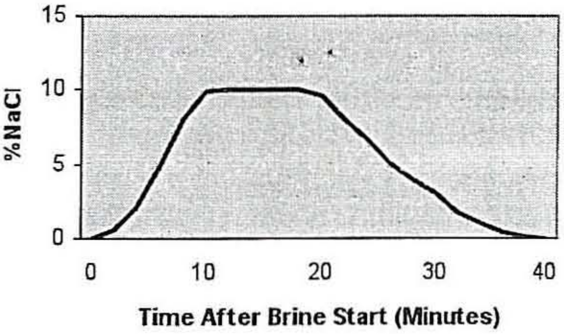
Short runs
Causes:
Water flow too low and
improper eduction.

concentration

Brine eductor plugged or sized incorrectly.

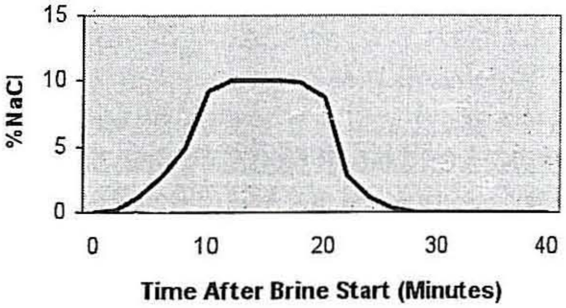
NOTE: Often overcome by additional time if problem cannot be corrected

F. Prolonged fast rinse



Hardness leakage
Causes:
-Incorrect valve setting
-Subfill disturbed
-Rinse channeling

G. Fast rinse



Wastes water
Causes:
Incorrect valve setting

8.0 Demineralization

8.1 INTRODUCTION

Demineralization means the removal of all soluble ionic material from water. The process is sometimes called deionization, but this is not strictly correct. Some ions remain from the ionization of water (chapter 1), and some organic material may also remain in the water. Ion exchange has been the standard method for producing demineralized water for many years. Recently, reverse osmosis has become an alternative tool for this purpose (see section 12).

Demineralization is required for certain higher-pressure boiler operations to minimize corrosion and deposition. Demineralized quality water is also required for direct feedwater attemperation for temperature control in superheaters and for direct injection of water and steam in gas turbines (see chapter 3). Many industrial processes, particularly in the pharmaceutical and electronics industries, also require the use of essentially pure water.

8.2 PRINCIPLES OF DEMINERALIZATION

Compared to the process of water softening, the demineralization process is somewhat different, but it employs the same principles. In this process, not only are calcium and magnesium ions replaced in the cation exchanger, but other cations are also replaced, and the anions, such as chlorides, nitrates, sulfates, bicarbonates and carbonates are replaced in the anion exchanger. Cations are replaced with hydrogen ions, and anions with hydroxide ions. The hydrogen and hydroxide ions generated in this process then react to form water, and the result is, at least theoretically, demineralized water.

8.2.1 Basic Demineralization Reactions

Demineralizer systems consists of one or more ion exchange resin vessels, which include a strong cation unit regenerated with hydrochloric or sulfuric acid instead of salt, and a strong anion unit regenerated with caustic. The cation resin exchanges hydrogen for cations in the raw water:

$$2RH + \begin{matrix} Mg^{+2} \\ Ca^{+2} \\ 2Na^{+} \end{matrix} = \begin{matrix} Mg \\ R_2Ca \\ 2RNa \end{matrix} + 2H^{+} \qquad (2\text{-}29)$$

where 'R' represents the cation exchange resin.

The anion resin then exchanges hydroxyl anions for the highly ionized anions as shown by these reactions:

$$2ROH + \begin{matrix} 2NO_3^{-} \\ SO_4^{-2} \\ 2Cl^{-} \end{matrix} = \begin{matrix} 2RNO_3 \\ R_2SO_4 \\ 2RCl \end{matrix} + 2OH^{-} \qquad (2\text{-}30)$$

In equation 2-30, 'R' represents the anion exchange resin.

8.2.2 The Basic Demineralization Process

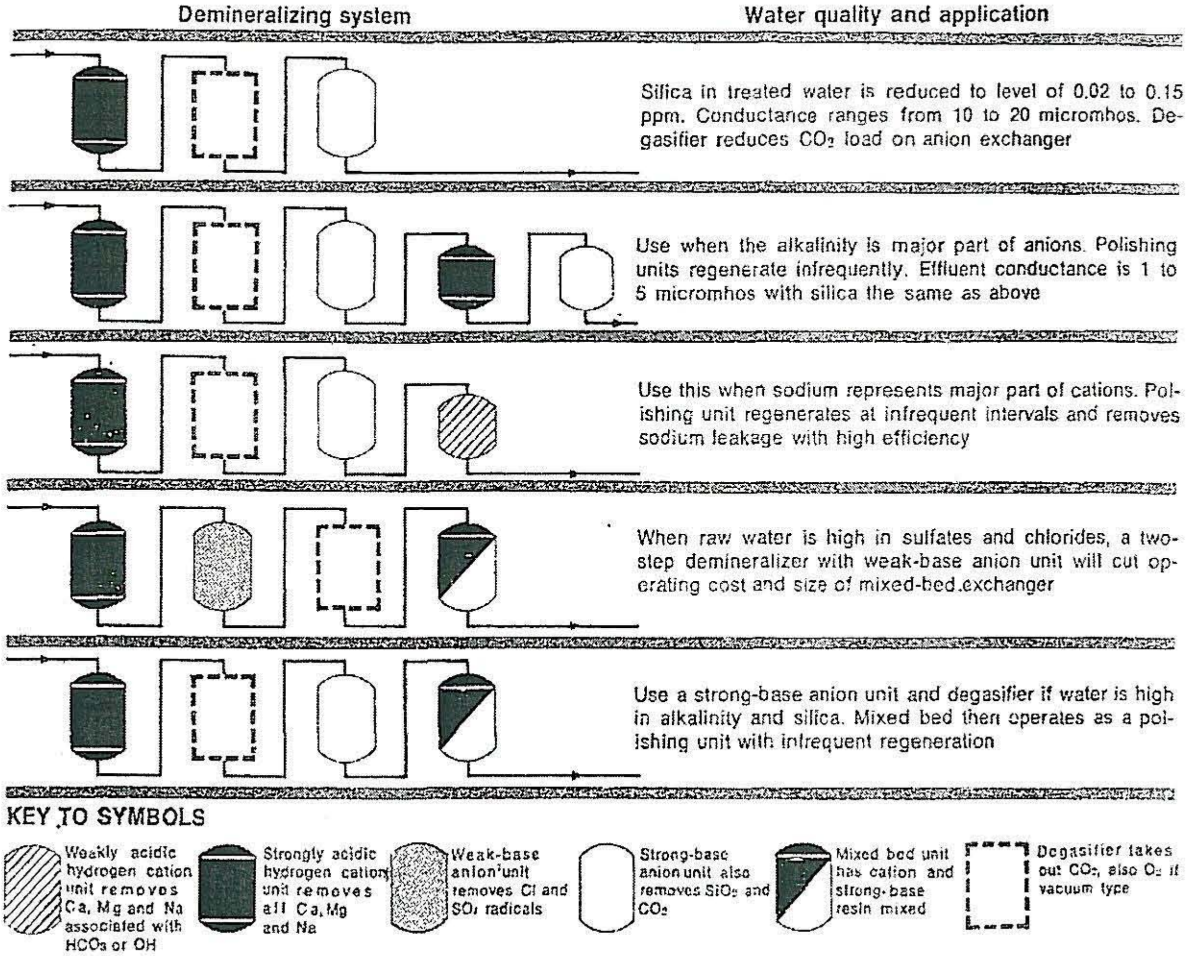
Raw water, first having been clarified and filtered to remove suspended solids, passes through a strongly acidic cation exchanger where the positively charged metal ions of the compounds dissolved in water undergo an exchange process with the available free moving hydrogen ions on the resin. These dissolved compounds, which are minerals, are converted into their corresponding acids as shown in equation (2-29).

The acid generated in the cation exchange unit (equation 2-29) is the free mineral acidity (FAH) in the water. This water now passes through a strongly basic anion exchange resin, that theoretically generates an equivalent amount of base to neutralize the FAH (equation 2-30).

8.3 ALKALINITY REMOVAL

Many raw water supplies intended for use as boiler feedwater contain substantial amounts of carbonate alkalinity (chapter 1).. Equilibrium calculations and practical experience have shown that it is often more efficient and cost-effective to take advantage of the volatility of carbon dioxide to strip alkalinity from the water, rather than neutralize it on the strong base anion resin. This has the added advantage of removing carbon dioxide that would otherwise enter the boiler system (chapter 3).

Several different schemes have been developed for dealkalizing boiler feedwater. Five common methods are illustrated in Figure 2-17. Specific schemes are site-specific, developed to match raw water quality with boiler design and operations. Two common feedwater dealkalization methods are discussed below; most others are variations on these basic schemes.



Silica in treated water is reduced to level of 0.02 to 0.15 ppm. Conductance ranges from 10 to 20 micromhos. Degasifier reduces CO_2 load on anion exchanger

Use when the alkalinity is major part of anions. Polishing units regenerate infrequently. Effluent conductance is 1 to 5 micromhos with silica the same as above

Use this when sodium represents major part of cations. Polishing unit regenerates at infrequent intervals and removes sodium leakage with high efficiency

When raw water is high in sulfates and chlorides, a two-step demineralizer with weak-base anion unit will cut operating cost and size of mixed-bed exchanger

Use a strong-base anion unit and degasifier if water is high in alkalinity and silica. Mixed bed then operates as a polishing unit with infrequent regeneration

KEY TO SYMBOLS

Weakly acidic hydrogen cation unit removes Ca, Mg and Na associated with HCO_3 or OH

Strongly acidic hydrogen cation unit removes all Ca, Mg and Na

Weak-base anion unit removes Cl and SO_4 radicals

Strong-base anion unit also removes SiO_2 and CO_2

Mixed bed unit has cation and strong-base resin mixed

Degasifier takes out CO_2, also O_2 if vacuum type

Figure 2-17: Five ways to demineralize water with cation and anion exchangers and degasifiers

8.3.1 Strong Acid/Strong Base Resins plus Decarbonator

A strong acid cation exchange resin converts all cations to free mineral acidity (equation 2-29). The acidity neutralizes bicarbonate alkalinity to form carbon dioxide, as in equation (2-31):

$$H^+ + HCO_3^- = CO_2\uparrow + H_2O \qquad (2\text{-}31)$$

The carbon dioxide is stripped from the water in a decarbonator (section 8.4, below). The water then flows to a strong base anion resin which exchanges anions for hydroxide and neutralizes the acidity (equation 2-32).

Because the anion resin used in the demineralizer is strongly basic, it will also remove weakly ionized carbonic and silicic acids, according to these reactions:

$$\begin{array}{lllllll} H_2CO_3 & & & & HCO_3 & & \\ H_2SiO_3 & + & 2ROH & = & 2RHSiO_3 & + & H_2O \end{array} \qquad (2\text{-}32)$$

The above reactions indicate complete removal of cations and anions from the water, but in reality, these are equilibrium reactions, and even with very efficient operation, leakage will occur. The leakage will vary according to the demineralizer system used.

8.3.2 Weak Acid/Strong Acid Cation Resins plus Decarbonator

Another way to remove alkalinity during demineralization is to pass the water first over a weak acid cation resin.

If a weak acid cation exchanger is installed, the incoming raw water is first passed through this unit. The resin reacts mostly with hardness associated with alkalinity, generating acid and forming carbonic acid:

$$2RCOOH + Ca^{+2} + 2HCO_3^- = (RCOO)_2Ca + 2H_2CO_3 \qquad (2\text{-}33)$$

As explained in chapter 1, carbonic acid is a very weak acid that dissociates readily to form carbon dioxide and water:

$$H_2CO_3 \;=\; CO_2\uparrow \;+\; H_2O \qquad (2\text{-}34)$$

Since the weak acid cation resin undergoes a slight exchange with the cations associated with the neutral salts, some free mineral acidity will also appear in the effluent along with the carbonic acids. The effluent from the weak acid cation exchanger, containing carbonic acid and some free mineral acidity, is then further treated in the strong acid cation exchanger. The reactions through the strong acid cation exchanger are the same as shown previously (equation 2-29), with the exception of alkaline compounds having already undergone an exchange in the weak acid cation exchanger.

The effluent of the strong acid cation exchanger, usually termed decationized water, can be passed through a decarbonator tower (section 8.4, below). Finally, the decationized and decarbonated water then goes through a strongly basic anion exchanger where anions are exchanged for hydroxide ions, the free mineral acidity is neutralized and residual carbonic acid and silicic acid are removed (equation 2-32).

8.3.3 Demineralized Water Quality

Water produced by any of these schemes and others is very high purity demineralized water. Sometimes a weak base anion resin is inserted before the strong base resin to help remove salts of dibasic acids that may have escaped the cation columns. The water leaving the strong base anion column is essentially pure for all practical purposes, but it still may contain a very minor level of dissolved substances. If very high quality water is needed, the anion effluent can be further demineralized, usually in a mixed bed column (See Section 9.0) where both cation and anion resins are mixed to polish the remaining impurities. Mixed bed demineralized water is needed for high-pressure boilers and some industrial processes. For boilers operating at pressures up to 1000 psi, mixed bed polishing generally is not needed.

8.3.4 Regeneration

After all the available ions in an ion exchanger are exchanged, the resin bed is exhausted. Any further continuation of the service run would not exchange any more ions. This is known as "total breakthrough capacity" of the resin bed. In practice, the service run is never continued to the breakthrough point. The service run is always terminated before the effluent quality falls below the acceptable quality. This is known as "operating capacity".

Regeneration of ion exchange resins is discussed in section 7.3.2. In demineralization trains, regeneration of both the weak and the strong acid cation exchangers is carried out with sulfuric acid, and the strong and weak base anion exchangers are regenerated with sodium hydroxide. This returns the resins to their original hydrogen and hydroxide forms, respectively (equations 2-29 and 2-30 running from right to left).

8.4 DECARBONATION

8.4.1 Principles

Decarbonators are simply packed towers in which a stream of air is used to strip dissolved carbon dioxide from the decationized water. The principle is the same as in boiler feedwater deaerators used to remove dissolved oxygen, except that deaerators usually operate hot and under pressure, with steam as the stripping gas (chapter 3), while most decarbonators operate with air at atmospheric pressure.

The operating principle of any deaerator or decarbonator is Henry's Law, which states that the concentration of gas in the liquid phase of any gas/water mixture depends upon the partial pressure of the gas in the vapor phase. A forced draft atmospheric decarbonator consists of a tank divided into a tower filled with plastic packing and a clearwell for storing the treated water.

Incoming water is sprayed over the plastic packing, forming a thin film on the surface. A centrifugal fan forces air up through the packing and over the film, stripping out carbon dioxide. The decarbonated water flows to the clearwell for further processing.

8.4.2 Operating Problems

Decarbonators are a possible source of contamination in the demineralization train. Due to the presence of a good supply of oxygen and flowing water, biological growth may occur on the upper tray sections of forced draft decarbonators. Hydroblasting the biological growth is an effective control measure. Periodic spraying with a dilute solution of an oxidizing biocide, usually sodium hypochlorite, is also effective. Obviously, the unit must be rinsed thoroughly with demineralized water before it can be returned to service.

8.5 DEMINERALIZATION EQUIPMENT

Demineralization systems vary according to the requirements of the application. As explained above, there are many system configurations consisting of combinations of resin types and decarbonator installation requirements. The piping, valves and fittings are made of lined or acid-resistant materials.

8.6 CONTROL TESTING

It is critical to ensure that all parts of a demineralization train are operating properly. Most modern systems are automatically controlled and regenerated based on site-specific system designs. In addition, plant operators run periodic control tests to monitor the systems. These control tests are shown in Table 2-15. Not all of these tests are run in all demineralization plants.

TABLE 2-15
Demineralizer Control Tests

Parameter	Weak Acid Cation (WAC)	Strong Acid Cation (SAC)	Weak Base Anion (WBA)	Strong Base Anion (WBA)
Weak acid cation	pH	Measures the drop in FMA near the end of the run.	<5	Normal Operation.
			>5	Unit close to end.
	Alkalinity	Test will measure the appearance of alkalinity leakage over and above the normal run alkalinity.	<10% Alk.	Normal leakage.
			>10% Alk.	Unit exhausted.
Strong acid cation	Free mineral acidity (FMA)	$SO_4 + Cl + NO_3$; Total mineral acidity less Na leakage.	Service FMA depends on raw water analysis. A 10% reduction in FMA is significant	Unit exhausted.
	Conductivity	Measures increased conductivity due to presence of FMA. Often measured as differential.		
	• Bed vs. effluent	Detects resin exhaustion approaching bottom of bed.	<5% variance	OK.
			>10% variance	Approaching end of run.
	• Unit effluent vs. header	Detects unit exhaustion compared to total header.	Value depends on number of units, e.g., the exhaustion of 1 out of 2 beds	When differential is detected, the exhaustion can be double-checked by pH.

			feeding a common header has a greater impact on the header quality than 1 out of 4 beds.	
	• Cation inlet vs. out	Allows variation in effluent conductivity.	Value depends on number of units, e.g., the exhaustion of one of the units.	When differential is detected, the exhaustion can be double checked by pH.
	pH	Normally not used as monitoring tool.	2 – 4	pH during normal operation is acidic.
			>4	End of run.
Weak Base Anion	Conductivity	Measures breakthrough of FMA.	<20 mmhos	Normal.
			>20	Breakthrough of FMA.
Strong Base Anion	Silica	Most useful test for breakthrough.	<0.5 ppm	Normal (120°F regeneration).
			0.5 – 2	Breakthrough of silica.
	Conductivity	Measures cation and/or anion breakthrough.	<20 umhos	Normal.
			>20	Breakthrough.

8.7 TROUBLESHOOTING

Table 2-16 is a guide to troubleshooting demineralizer systems. See Section 8.0 for information on elution studies. Of course, with elution studies on demineralizer systems, acid or caustic concentration during the cycle is tested rather than chloride. Due to the materials, exercise extreme caution in handling samples and follow plant safety requirements.

The information in Table 2-16 will be helpful in understanding problems in demineralization trains and in working with your customers to solve these problems.

Table 2-16. Demineralizer Troubleshooting Guide
(Strong Acid Cation/Strong Base Anion Resins)

Problem	(i) Causes	(ii) Corrective Action
Cation Units		
Short Runs	Change in raw water.	Check raw water analysis. Change source of raw water or increase regeneration level.
	Deteriorating regeneration practice.	Review regeneration elution study. Readjust acid and/or rinse flows based on review and elution study.
	Channeling due to bed fouling.	Check influent turbidity from clarifier or lime softener. Improve clarifier or softener performance. Check for biological contamination. Remove biological growth and sterilize the bed. Bed inspection.
	Channeling due to distributor blockage.	Vessel inspection. Repair or replace distributor or strainer.
	Resin fouling.	Resin analysis. Reduce source of foulant, clean up resin. Upset subfill. Correct source of upset and rebed subfill.
High Average Leakage • Increase in sodium leakage, accompanied by lower FMA, lower cation conductivity, higher anion conductivity.		Check charge in raw water and regeneration procedure.
	Raw water bypassing unit.	Check hardness and sodium increase. Replace faulty valve.

	Previous complete exhaustion.	Check throughput information. Double regeneration.
• Hardness and increased sodium leakage.		Check raw water bypass valves.
• Hardness leakage		Testing mistake. Neutralize sample to pH 7 before test.
	Resin fouling.	Check for $CaSO_4$. Correct acid profile during regeneration will prevent $CaSO_4$ precipitation. Check for $CaCO_3/Mg(OH)_2$ and carryover from precipitation softener.
	Polymer carrythrough.	Check overdose of cationic polymer in clarifier. Reduce polymer dosage or add clay for increased suspended solids.
Anion Units		
Anion Short Runs		
	Organic fouling.	Do resin analysis. Resin cleaning, if needed.
	Loss of salt splitting capacity.	Do resin analysis. Increase regeneration level or rebed. Check raw water analysis on regeneration procedures and channeling and resin loss.
	Poor quality caustic.	Check Caustic silica analysis. Try to obtain higher quality caustic, if needed.
High Average Leakage	Check for loss of salt splitting capacity.	
	Deteriorating temperature control in regeneration system.	Check temperature elution profile. Get Instrument Department to look at temperature control loop.

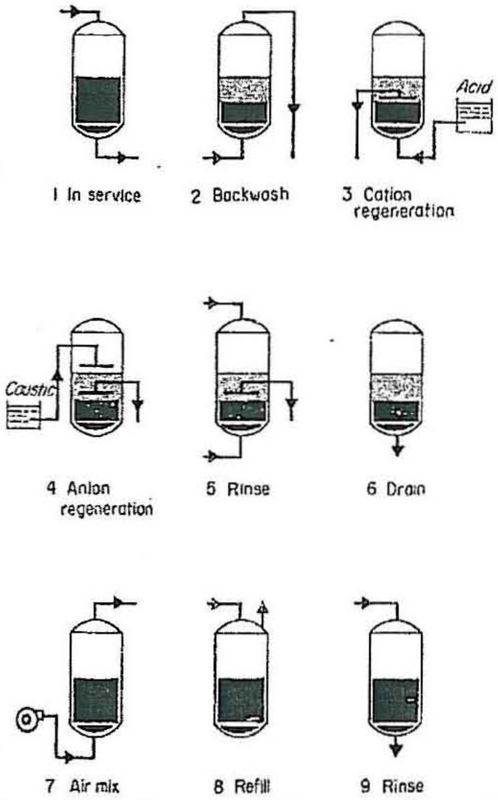
	Water by-passing unit.	Check valves and resin.
	Presence of cation resin in anion unit due to mechanical failure of cation underdrain.	Check resin bed and vessel.
	Previous complete exhaustion.	Check flow and double regenerate.
Hardness in Anion Effluent	Fouling of anion due to problem with cation leakage.	Do resin metals analysis Chemical cleaning after cation problem has been rectified, if needed.
	Poor quality caustic.	Check caustic hardness analysis. Try to obtain a better quality caustic, if required.

8.8 MIXED BED DEMINERALIZATION

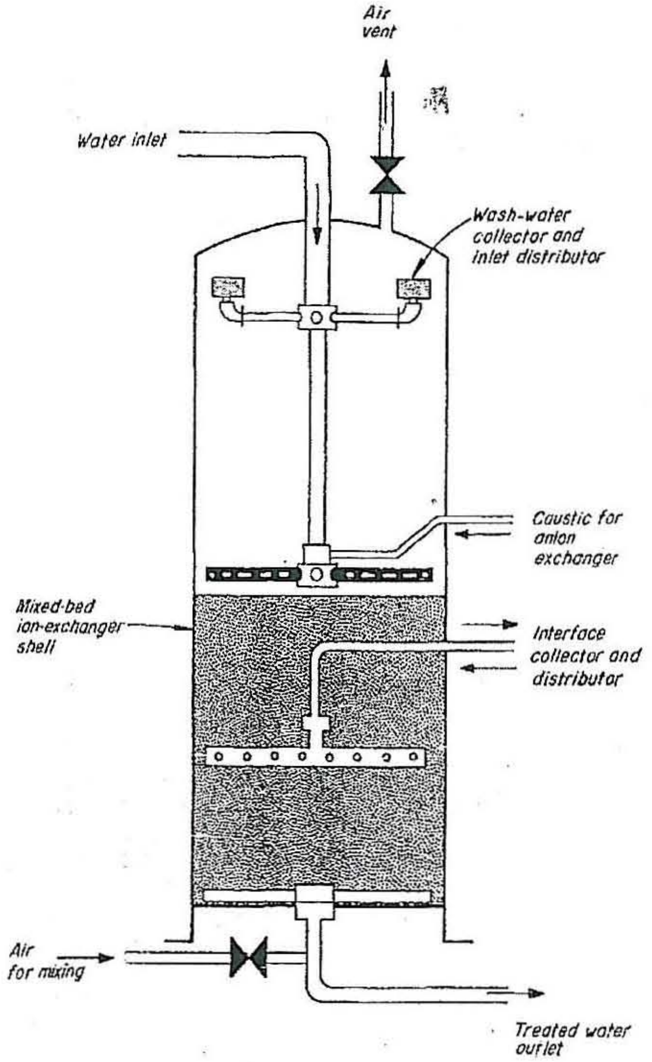
As explained earlier in this section, mixed bed systems, containing both strong acid cation and strong base anion resins in the same tank, are installed as polishing units to remove the expected leakage of sodium and silica in the anion effluent when the highest possible purity demineralized water is needed. Also, in certain instances, where the high purity water requirement is small and the total dissolved solids level in the makeup water to be treated is low (usually less than 200 ppm), mixed bed demineralization may be employed as the only form of demineralization. This is referred as makeup mixed bed demineralization.

8.8.1 Equipment

Figure 2-18 is a schematic drawing of a typical mixed bed demineralization unit. A mixed bed demineralizer column is similar to a conventional cation or anion unit, but with significant differences:



Regeneration of mixed resin bed is illustrated from initial backwash to end of rinse and return of unit to service. Light shading represents lighter anion resin, dark tint is heavier cation beads. Entire process can take anywhere from two to four hours



Mixed-bed demineralizer houses intimate mixture of cation- and anion-exchange materials. Anion beads grab acid produced by cation beads, allowing reaction to go almost to completion. Air for mixing enters through distributor near bottom

Figure 2-18
Mixed Bed System

- There is an extra lateral assembly midway up the bed.
- Two sight glasses are installed in the vessel shell. One is at the top of the bed; the other at the location of the extra lateral.
- Provision for the introduction of a large quantity of air is required.
- The shell is slightly higher to allow more room for backwash expansion.

8.8.2 Effluent Expectations

The intimate mixing of strong acid cation and strong base anion resins in mixed bed demineralizer permits excellent contact with trace leakage of carbonic and silicic acids, and sodium. Table 2-17 shows expected water quality that can be achieved with a properly run mixed bed demineralization system:

Table 2-17. Expected Mixed Bed Effluent Water Quality

Parameter	Effluent, mg/L
TDS, ppm	<0.001
Conductivity, mmhos	<0.1
Silica (SiO_2), ppm	<0.01
pH	7

The leakage through a mixed bed column is considered to be independent of the influent water composition. However, the capacity of the bed is very dependent on influent water quality.

The pH of the mixed bed effluent is a theoretical value. The pH is very difficult to measure because of the low conductivity of the water (chapter 1). In spite of all efforts, there may be a slight amount of organic contamination leaking through the bed.

The intimate mixing of cation and anion beads in a mixed bed is optimized for leakage considerations. This arrangement reduces the available capacity of each individual resin. Normal design capacity is 8 kilograins/ft^3 at 5–8 gpm/ft^3. This capacity will decrease as the flow rate increases.

8.8.3 Regeneration Practices

Regeneration practices must be specifically designed for mixed bed systems. Reviewing these procedures is a good way to understand how mixed bed systems function. The backwash process is illustrated in Figure 2-18.

- Backwash: The backwash step serves to separate the cation from the anion material. The heavier cation resin settles to the bottom of the vessel and the anion resin layers above it. The backwash step usually proceeds for 20 to 30 minutes to insure separation.
- Settling Step: After the backwash, the bed settles for 5 to 15 minutes. This is the best time to inspect the mixed bed for bed height and demarcation between cation and anion resins.
- Acid Introduction: Sulfuric acid at 4–8% is introduced from the bottom of the unit and removed at the mid-bed take-off lateral (interface collector). A strong concentration of acid (10–12 lbs. per cu. ft.) can be used since there is no danger of calcium sulfate precipitation. However, in a makeup mixed bed, where hardness is present, sulfuric acid must be introduced in a stepwise fashion to avoid calcium sulfate precipitation.
- Caustic Introduction: Caustic may be introduced simultaneously with, or after the acid step. Caustic is introduced through the lateral above the anion bed and removed through the interface collector. When caustic is introduced after the acid step, an upflow blocking of water through the cation resin is used to prevent sodium hydroxide from migrating into the

cation bed. Caustic is introduced at 4% and 120°F for optimal silica control; the dosage is approximately 10 – 15 lbs/ft^3.

- Rinse: Displacement rinses are conducted in the same direction as the regenerant flow. A fast rinse is then applied to the entire bed in a downflow fashion from the service inlet. The fast rinse is normally interrupted after 5 or 10 minutes for the air mix.
- Drain: The level of water in the unit is allowed to drain to a point 6 to 8 inches above the top of the anion bed. At the point, the air mix commences.
- Air Mix: The air mix restores the random mixing of the two resin types. Air is supplied in an upflow fashion from the service outlet distributor. Generally, 10 SCFM/ft2 at 10–15 psi are required to properly mix the bed,
- Final Rinse: After the air mix step, the bed is rinsed to acceptable conductivity.

The control system to accomplish the above regeneration sequence is quite complicated. This and the extra mid-bed lateral contribute to the high capital cost of mixed bed demineralizers.

8.8.4 Control Testing

As with other systems, an understanding of operator control procedures for mixed bed demineralization columns is helpful in working with customers to solve problems. Typical control tests are listed in Table 2-18.

TABLE 2-18

Mixed Bed Control Tests

Test	Function	Test Results	What the Test Result Shows
Conductivity	Measures TDS of effluent	< 0.1 mmho (conductivity)	Acceptable Performance
		> 10 megohms (resistivity)	
		> 0.5 mmho, < 2 megohms	End of run
SiO_2	Usually by continuous analyzer	< 0.01 ppm	Acceptable Performance
		> 0.05 ppm	End of run
pH		7	Theoretical pH of effluent
		With conductivity > 1 mmho:	
		pH > 7	Cation exhausting or cation layering at bottom of unit
		pH < 7	Anion exhausting or organic acid contamination

8.8.5 Troubleshooting

Table 2-19 is a troubleshooting guide for mixed bed demineralizers.

TABLE 2-19

Mixed Bed Troubleshooting

Problem	Possible Causes	Checks	Action
SHORT RUN – (Acceptable quality water produced during the run; premature breakthrough.)			
	Sampling Error	Sampling$_{(1)}$ Procedure.	Must use in-line probe.
With pH > 7	Deteriorating cation regeneration.	Review regeneration procedure.	Correct flows and/or times.
	Loss of cation resin.	Level of resin interface after backwash.	Add cation resin.
With pH < 7	Organic acid contamination.	Organic fouling of anion.	Clean or rebed anion.
	Deteriorating anion regeneration.	Regeneration review, elution study.	Correct flows and/or times.
	Loss of anion resin.	Level of top of bed.	Add anion resin.

HIGH AVERAGE CONDUCTIVITY – (Unacceptable quality water produced during run; may or may not be accompanied by premature breakthrough.)

(a) Makeup Mixed Bed (b) Polishing Mixed Bed	Influent by-passing unit.	Presence of hardness in effluent indicates raw bypass.	Repair faulty valve.
With pH > 7	Influent by-passing unit.	Check Na/SiO_2 ratio in influent (primary anion effluent) and mixed bed effluent.	Repair faulty valve.
With pH < 7	Cation layering at bottom of unit.	Water level too high after drain-down.	Increase duration of drain-down.
	Air mix inadequate.	Duration of air mix.	Increase timer setting for air mix step.
		Vent too small.	Increase valve/piping size.

HIGH AVERAGE SILICA

	Caustic temperature too low.	Temperature(2) profile during regeneration.	Correct dilution water heater system.
	Water by-passing unit.	Check by-pass.	Repair valve.
	Degraded anion resin.	Resin analysis.	Rebed as needed.
	Organic fouling of anion.	Resin analysis.	Clean or rebed resin.

LONG RINSE-DOWN

	Degraded/fouled resin	Resin analysis	Rebed or clean.

Notes:

(1) In analyzing ultrapure water, special precautions must be taken to prevent contamination of the sample.

(2) Caustic and acid combine together in a simultaneous regeneration to give a misleadingly high regenerant effluent temperature.

8.8.6 Inspection Procedures

Location of the resin interface, location of the top of the bed, and the amount of water in the unit after drain-down are key points to check.

- Resin Level: Observe the resin level in the two sight glasses after the settling step following the backwash.

- <u>Lower Sight Glass</u>: Using a light, determine the resin interface. With older resins, two different shades of brown may be seen. The demarcation between resins should be level and within ±1 inch of the center of the lower sight glass.
- <u>Upper Sight Glass</u>: Using a light, examine the location of the top of the bed. It should be level and within ±1 inch of the center of the upper sight glass.
- <u>Drain</u>: At the end of the drain step the water level should be within 4 to 6 inches of the top of the resin bed. The level should be visible at or just above the top of the sight glass. If the water level is not visible, there will be too much water remaining in the unit after the air mix. This allows the heavier cation resin to accumulate at the bottom of the unit. The cation rich layer will adversely affect water quality. If too little water remains after the drain, the air mix will not be effective.

9.0 Condensate Polishing

9.1 INTRODUCTION

Condensate polishing refers to the use of pretreatment technology, as discussed in this section of the Manual, in the preparation of returned boiler condensate for reuse as boiler feedwater.

The use of condensate polishing has become more important as feedwater quality and boiler systems pressures have increased. Typically, the contaminants in high pressure boiler condensate are iron, copper and low levels of soluble salts. Most common types of condensate polishers are relatively simple filters and sodium zeolite polishers that function primarily as filters. In some cases, when the condensate is from process steam, further treatment may be needed, i.e. activated carbon to remove organic matter, or biocides or ultraviolet light for sterilization.

9.2 TYPES OF POLISHING SYSTEMS

As explained earlier in this chapter and in chapter 3, condensate polishing is used to remove impurities from returned steam condensate so that it can be reused as boiler feedwater.

Types of condensate polishing systems are shown in Table 2-20. Condensate polisher effluent is frequently guaranteed to deliver either 30 ppb of total iron and copper, or 10% of the inlet amount, whichever is greater.

TABLE 2-20

Condensate Polishing Systems

			Systems				
Contaminant	**Form**	**Source**	**Sodium zeolite**	**Cellulose precoat**	**Magnetic**	**Deep bed mixed bed**	**Precoat mixed b**
Fe and Cu oxide	Insoluble "Crud"	Condensate corrosion	Yes	Yes	Yes	Yes	Yes
Iron hardness	Soluble	Condensate corrosion, makeup contamination	Yes	No	No	Yes	Yes
TDS	Soluble	Cooling water inleakage, process contamination	No	No	No	Yes	Yes
Oil/Organic	Insoluble	Process, coolers	No	Yes	No	No	Yes

9.3 POLISHING FILTERS

9.3.1 Precoat Filtration

In this type of condensate polisher, the filtration medium, normally diatomaceous earth or fine sand, is added to the unit in the form of a slurry of fine mesh (60 – 600 mesh). The unit contains several columnar sleeves, which are covered with a screening, which will retain the fine mesh material. When the filter medium slurry is added to the unit, water is withdrawn and the slurry particulates are retained on the screen in the form of a thin layer. The layer, called the precoat, may be only 1/8 to 1/4 inch thick, but it serves as an excellent filter due to the fine mesh of the medium. In addition, this design also removes significant oil contamination.

After service, the coating on the septa is removed by reversing or backflushing the flow of water through the columns. This breaks up the coating, which is then discarded. A fresh slurry of material is then added to the unit and the cycle repeats. New medium must be used for each cycle; it is not the practice of the industry to recover spent precoat medium.

9.3.2 Magnetic Filters

Magnetic filters consist of a vessel containing a magnetizable medium, called the matrix. When an external field is applied, high strength magnetic fields are set up within the matrix. Magnetic particles (iron and copper oxides) are effectively trapped in the matrix. Removal of more than 90% of particulate iron oxides has been reported; removal of over 80% of copper oxides is attainable. Effluent levels average less than 20 ppb iron and less than 5 ppb copper.

Magnetic filters normally run for 12 hours between cleanings. Cleaning consists of demagnetizing the matrix, followed by a quick backwash, usually less than one minute long. Because of the quick cleaning step, only one unit need be employed in a system. Condensate is bypassed around the unit for the one minute cleaning step.

9.4 ION EXCHANGE POLISHING

Two forms of mixed bed condensate polishing are practiced in the industry: deep bed and powdered resin. Simple sodium zeolite resins are also used, serving as both ion exchange columns and particulate filters.

9.4.1 Deep Mixed Beds

Deep bed condensate polishers refer to 2 to 4 ft. deep beds of mixed cation/anion resin. The units generally contain additional internal bracing for the laterals due to the high flow rates used. The flow rate range for deep bed units is 30 to 100 gpm/ft^2; 50 gpm/ft^2 is the usual rate.

9.4.2 Precoat Mixed Beds

Mixed bed resin can be pulverized to 100 to 600 mesh and used in a precoat application as discussed in section 9.3.1. In this fashion, the resins perform as excellent filters and also offer limited ion exchange capacity. Due to the thin layer of resin comprising a precoat filter, the available capacity is quite small, but still provides ion exchange capacity for soluble contaminants in the ppb range. In the event of a large condenser leak, precoat ion exchange units would exhaust within a few minutes.

9.4.3 Sodium Cycle Polishers

This form of condensate polisher is typically seen in industrial boiler systems. The ion exchange resin is a strong acid cation exchange resin operated in the sodium cycle (section 7.0). It acts both as a resin to remove soluble iron, copper and hardness, and as a filter to trap insoluble metallic oxides. In this application, the flow rate is commonly 20 to 30 gpm/ft^2. This is higher than conventional sodium zeolite applications because:

- Particulate removal in the bed and mat-filtration on top of the bed are enhanced by higher flow rates.
- At higher flow rates, cross-sectional throughputs are increased and installation costs reduced.
- Due to the low ionic loading, kinetics is not a prime design factor and higher flows can be tolerated.

Key design features include:

- Unlined steel tanks fitted with a corrosion-resistant underdrain and wrapped laterals.
- Top inlet water distributor designed for high service flow rates at low-pressure losses.
- Brine regeneration and simple chemical cleaning equipment.
- Inlet and outlet piping and valves large enough to handle high service flow rates without excessive pressure loss.
- Backwash and rinse valves and piping with equipment to prevent flashing of hot condensate.
- The resin is regenerated with 10 – 15 lbs. of NaCl/ft^3. Sulfite at 0.25 lb./ft^3 is used with the brine during regeneration to prevent iron in the resin from precipitating due to reaction with dissolved oxygen.

In the sodium cycle, the resin will react with neutralizing amines used for condensate corrosion control (chapter 3). The reaction is not stoichiometric, but enough Na can be released from the resin to interfere with coordinated PO_4/pH boiler programs. In addition, amine exchanged onto the resin is not available for recycle to boiler feedwater. To alleviate these problems, the resin can be operated in the amine form. See chapter 3 for more on this subject.

9.5 CONTROL TESTS

For non-mixed bed condensate polishers, the unit performance can be monitored by particulate or total iron and copper. Pressure drop is also commonly used to determine when a unit should be taken off-line.

For mixed bed condensate polishers, pressure drop is also employed, but because of the additional chemistry that a mixed resin bed can impart, conductivity and continuous silica monitoring are used.

10.0 Reverse Osmosis

10.1 INTRODUCTION

Osmosis is a natural process that causes water to flow through a semipermeable membrane from a dilute solution on one side to a more concentrated solution on the other side, thus diluting the concentrated solution. Osmotic flow will continue until both solutions are at equal ionic concentrations. Osmotic pressure is the natural pressure difference that provides the driving force for osmotic flow of fluids across membranes.

All living things depend upon osmotic forces. Plants and animals absorb water, and animals separate liquid waste for discharge, by osmosis. Osmotic membranes are said to be semipermeable because they allow water to flow through the pores but not soluble ions.

Osmotic pressure can be demonstrated as shown in Figure 2-19. The difference in fluid height between the two compartments is related to the osmotic pressure. Osmotic pressure is a function of the solute loading of the concentrated solution, i.e., the higher the concentration, the higher the osmotic pressure. The movement of water across the membrane continues until the system reaches equilibrium: that is, until the head pressure caused by the increasing height of the column of concentrated solution equals the osmotic pressure driving water across the membrane.

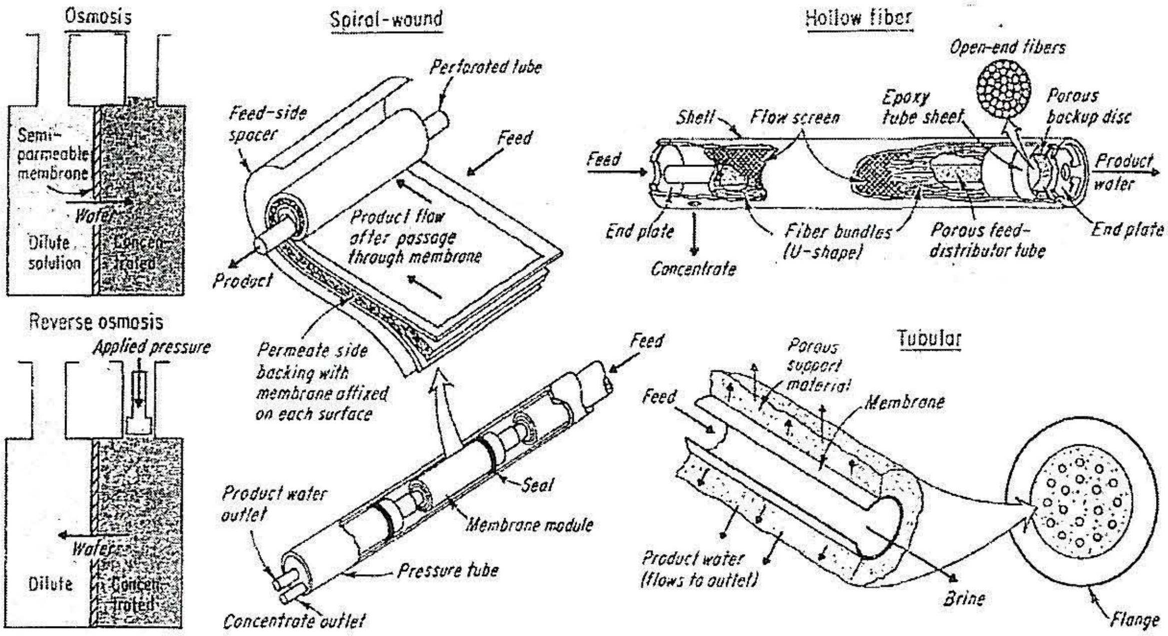


Figure 2-19
Osmosis and Reverse Osmosis

Reverse osmosis, as the name implies, is simply a reversal of normal osmotic flow, as shown in Figure 2-19. Pressures much higher than osmotic pressures are applied to concentrated water solutions. This, in effect, squeezes water backwards through the membrane, creating pure water on one side (the permeate) and a more concentrated solution on the other side (the concentrate or reject water).

Reverse osmosis (RO) was originally developed as an alternative to distillation of seawater. Today, RO units large and small provide high quality drinking water and boiler feedwater to ships of all sizes and to arid countries in the Mideast and elsewhere.

Over the last several years, low-cost, efficient membranes and the increasing costs of demineralization have made RO a good choice for producing high-quality water. Common applications of RO include potable water production, boiler feedwater preparation, cooling tower blowdown treatment, computer and pharmaceutical industry ultrapure water use and wastewater treatment.

10.2 PRINCIPLES OF REVERSE OSMOSIS (RO)

Figure 2-19 also shows, schematically, how an RO membrane works in a continuous RO process and how membrane assemblies are prepared.

Pressurized feedwater travels tangentially along the membrane surface. Material that passes through the membrane is called permeate or product water. Permeate travels perpendicularly through the membrane cross-section. Material that does not pass through the membrane is called the concentrate, reject or brine.

The ability of a membrane to pass water and retain salts is quantified by recovery and rejection. Recovery represents the portion of feedwater that is "recovered" as permeate. Rejection describes the ability of the membrane to retain salts.

$$\%\ \text{Recovery} = \frac{\text{Product flow} \times 100}{\text{Feed flow}} \qquad (2\text{-}35)$$

$$\%\ \text{Rejection} = \frac{(\text{Feed conc.} - \text{Product conc.}) \times 100}{\text{Feed concentration}} \qquad (2\text{-}36)$$

The term salt passage is sometimes used to quantify the amount of salt that passes through the membrane. Salt passage is determined as follows:

$$\%\ \text{Salt passage} = 100 - \%\ \text{Rejection} \qquad (2\text{-}37)$$

$$\%\ \text{Salt passage} = \frac{\text{Product concentration} \times 100}{\text{Feed concentration}} \qquad (2\text{-}38)$$

Concentration factor is sometimes used to describe the degree to which the salts that are retained by the membrane are cycled up in concentration. The concentration factor can be easily approximated as feed volume divided by concentrate volume.

10.3 SEMI-PERMEABLE MEMBRANES

10.3.1 Membrane Compositions

The two most common membrane materials used in water purification are cellulose acetate (CA) and polyamide. Membranes made from these materials have a non-porous "skin" layer integrated onto a microporous support layer.

Cellulose acetate membranes are made of cellulosic material. Polyamide membranes are a composite structure of two materials: a microporous support layer, typically polysulfone, onto which a thin skin, typically made of polyamide, is applied. Because polyamide membranes are a composite of two materials with a thin-film non-porous layer, they are commonly referred to as thin-film composite (TFC) membranes.

10.3.2 Membrane Comparisons

Table 2-21 shows the significant differences in the properties and performance of CA and TFC membranes.

TABLE 2-21
Characteristics of Cellulose Acetate (CA) and Thin-Film Composite (TFC) Membranes

Property	CA Membrane	TFC Membrane
Surface	Smooth	Rough
Surface Charge	Neutral	Negative
Typical Operating Pressure, psig (brackish feedwater)	300-600	150-400
Maximum Temperature, °C	35	45
pH Range	4-6	2-10
Maximum Free Cl_2, ppm	1.0	0
Expected Lifetime, yr.	2-3	2-5
Hardness, Typical Rejection	96%	97%
Sodium, Typical Rejection	95%	96%
Sulfate, Typical Rejection	99%+	99%+
Silica, Typical Rejection	85%	98%

TFC membranes offer two advantages over CA membranes: they can be operated at lower pressure and they can be used over a broader pH range. However, due to their rough surface, TFC membranes are more easily fouled by suspended solids (colloids), organics, and biological materials. In addition, because TFC membranes are sensitive to chlorine, it is difficult to control microbiological growth. Since these membranes have a negative surface charge, cationic polymer feed must be controlled more carefully. CA membranes are more forgiving with respect to fouling and their chlorine resistance makes biological growth control more straightforward.

10.3.3 Membrane Modules

RO membranes are modularized for compactness and ease of use. Module configurations include plate-and-frame, tubular, spiral-wound and hollow-fiber designs. Modules allow for the replacement of portions of damaged or fouled membrane without replacing all the membrane in a given system.

Spiral-wound and hollow-fiber membrane modules (Figure 2-20) are the most common configurations used in water purification. Spiral-wound modules consist of several flat sheets of membrane, each of which is folded in half, feed side to feed side. A polymeric mesh feed spacer is used to separate the folded-over feed sides from each other. The entire assembly is then wrapped around the permeate tube. In RO systems, several membrane modules are placed in series in pressure vessels called tubes, as in Figure 2-20.

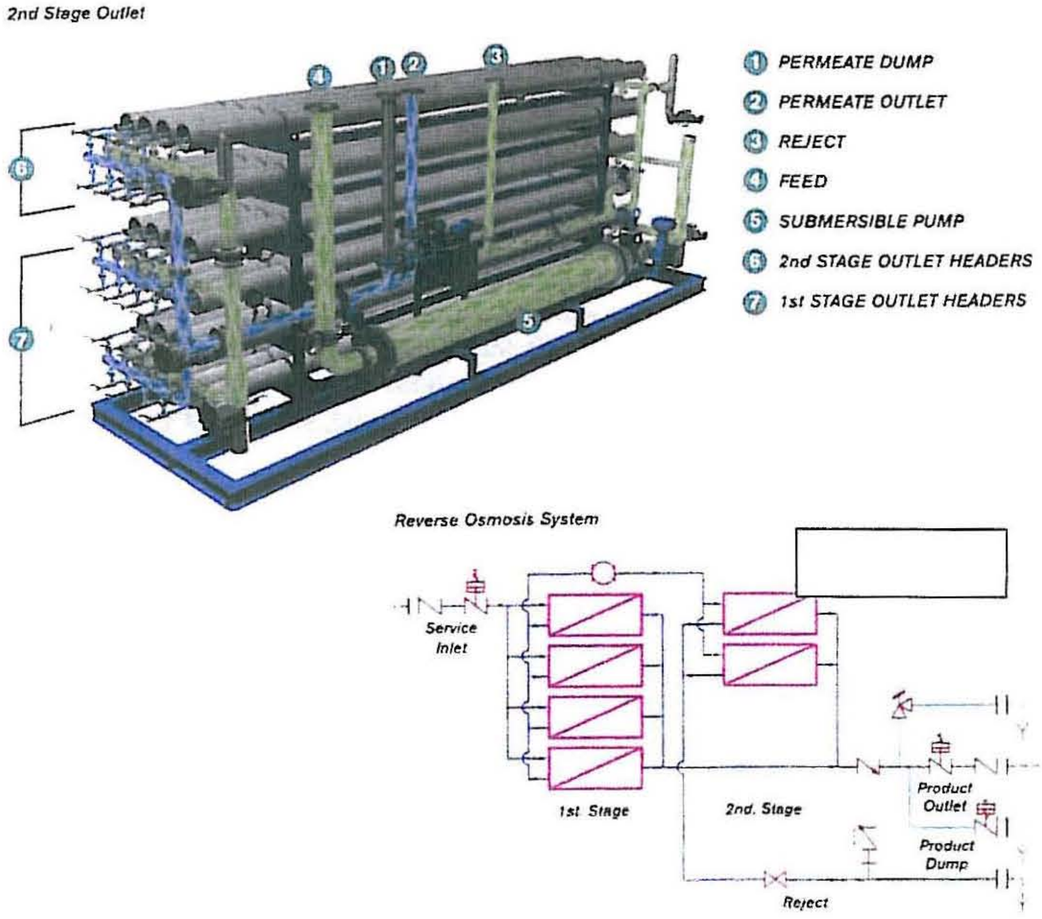


FIGURE 2-20

Typical RO membrane module assembly

Feedwater enters the module at one end and travels down the axis of the module through the channel created by the feed spacer. Concentrate exits the module at the end opposite the feed. Permeate is captured in the permeate spacer and spirals into the permeate tube. The permeate exits the module out of the end of the permeate tube.

Hollow-fiber modules use membranes that are in the form of hollow fibers. The feed side of the membranes is on the outside of the fibers. The fibers are looped and the ends are potted in a resin for rigidity as well as to separate the feedwater from the permeate. The fiber bundle is housed in a pressure vessel. Feedwater enters the module shell-side, travels around and through the fiber bundle, exiting the module shell-side at the opposite end. Permeate travels through the fibers into the hollow centers and exits out of the module through the potted end of the fibers.

The productivity of an RO train is a function of the desired permeate flow and the physical size available to place the system. Additional trains may be added to increase overall productivity.

10.3.4 Membrane Fouling

Serious RO operating problems can result from inadequate feedwater quality. Special procedures are required to provide the necessary water quality and protect the membranes.

Membranes are easily fouled by particulates such as:

- Suspended solids
- Colloidal (non-reactive) silica
- Iron oxide
- Long-chain, high molecular weight organics (e.g., humic acids)
- Microbes that feed on organic matter. Foulants can be entrained on the feed spacer in the membrane module and/or trapped on the surface of the membrane itself. The rough surface of TFC membranes readily traps particulates, organics, and microorganisms, making these membranes more susceptible to surface fouling than CA membranes, which have smooth surfaces.

Both colloidal and reactive silica and both particulate and soluble iron cause problems in membrane systems. Colloidal silica will foul membranes while reactive silica can polymerize and scale membranes as discussed below. Particulate iron will foul membranes. Soluble iron will also foul since ferrous iron will oxidize and precipitate within a membrane module under the pH and dissolved oxygen levels typically found in RO feedwater.

Particulate foulants usually affect the membranes in the first stage of an RO system, although organics and microorganisms can be found in all stages. Fouling will effect RO system performance in these ways:

- Decrease productivity
- Increase the pressure drop through the system
- Increase the potential for additional fouling
- Reduce product purity

Decreases in productivity are sometimes masked by increasing the feed pressure. Refer to the discussion on normalization for details. Higher feed pressure and high pressure drops will result in physical damage to the membranes.

Tests that can be used to measure potential membrane foulants include:

- Silt density index (SDI) – see section 10.3.5.
- Turbidity
- TOC
- MB plate counts
- Elemental analysis

10.3.5 The Silt Density Index (SDI)

The Silt Density Index (SDI) is a test developed specifically to determine the general suspended solids fouling potential of RO feedwater. Membrane manufacturers' warranties require an SDI less than 5. Higher feedwater SDI values almost invariably lead to performance problems in an RO unit. SDI measurements should be taken frequently, from every shift to every day on surface water sources, much less frequently on ground water sources.

The test involves filtering a standard sample of feedwater under controlled conditions and measuring the deposit on the filter pad. Detailed procedures can be found in ASTM Specification D 4189-82. Deposits on the filter pads used in the SDI test should be analyzed to determine their composition so that appropriate techniques can be employed to remove these suspended solids from the RO feedwater.

10.3.6 Membrane Degradation

To prevent degradation of the membrane, temperature, pH, and chlorine limits are all controlled. Note that TFC membranes are degraded by all oxidizers at a rate proportional to the strength of the oxidizer, its concentration, and the contact time. CA membranes can tolerate low levels of free halogen.

In addition to temperature, pH, and oxidizers, many solvents also will degrade membranes by solubilizing the membrane polymer. Each membrane is sensitive to solvents for specific polymer(s) used to prepare the membrane.

Degradation will affect membranes in all stages of an RO system with the lead modules in the first stage degraded most severely. Once the membrane polymer has degraded, performance usually cannot be restored. A degraded membrane will exhibit higher water throughput and lower salt rejection.

- RO feedwater temperature is not usually controlled due to the lack of appropriate streams for heat exchange or due to the costs associated with maintaining heat exchangers. Therefore, streams with temperatures in excess of temperature limits are usually not treated with RO.

Sulfite (typically sodium metabisulfite) is the preferred method for dechlorinating feedwater. A non-cobalt catalyzed bisulfite product should be used. Sulfite feed rates should provide for a safety margin of 2 to 3 times the stoichiometric amount required (see Table 2-22). Ideally, bisulfite should be fed after the cartridge filter to minimize microbiological growth in the filter. A minimum contact time of 20 seconds is required. Therefore, bisulfite should be fed after the cartridge filter only if enough contact time is available between the filter and the RO membranes.

TABLE 2-22
Bisulfite Feed Rates To Reduce Chlorine

Compound	Stoichiometric dose ppm/ppm chlorine	Safety dose ppm/ppm chlorine
Sulfite	1.77	4.5
Bisulfite	1.46	3.5
Metabisulfite	0.70	2.0

Activated carbon is not recommended as the first choice for dechlorination. Activated carbon can promote microbiological growth if the media is left in service for too long, leading to microbiological fouling of RO systems. Carbon fines can also foul membrane modules.

10.3.7 Organic and Microbiological Problems

Some naturally-occurring high molecular weight organic matter can be broken down with chlorine. To minimize fouling due to organics and microorganisms, it is recommended that RO feedwater be chlorinated and carry a residual through as much of the pretreatment system (including tanks) as possible.

CA membranes can tolerate up to 1 ppm free chlorine continuously and should be operated with a residual of 0.05 ppm in the concentrate. RO feedwater to a TFC membrane must be dechlorinated to prevent membrane degradation as discussed below. If possible, the water should be dechlorinated with sodium sulfite after the final filters to minimize microbiological growth in the filters.

Although carbon filters are commonly used to remove organic matter and chlorine from boiler feedwater, their use to treat RO feedwater should be carefully considered. Activated carbon can promote microbiological growth if the media is left in service for too long, leading to microbiological fouling of RO systems. Carbon fines can also foul membrane modules.

10.3.8 Mineral Scale Formation

Scaling occurs when the concentration of a dissolved solid exceeds its solubility limit. Solubility is a function of solute concentration, pH, and temperature (chapter 1).

Common scales include:

- Reactive silica (which can polymerize and scale RO membranes)
- Calcium carbonate
- Sulfate scales of barium, strontium, and calcium

Barium and strontium sulfate scales have very low solubilities. Once formed, these scales are virtually impossible to remove from a membrane. The potential for sulfate scale is increased when sulfuric acid is used to adjust pH.

Since the dissolved solids concentration in the reject water increases as more and more water is recovered by the RO system, scaling usually occurs in the last stage of the system. The effect of scale on the performance of an RO system will be similar to that described above for fouling.

Elemental analysis of the RO feedwater is used to test for scale-forming materials. The calcium carbonate scaling potential can be estimated by calculating the Langelier Saturation Index (LSI) or Stiff-Davis Saturation Index (SDSI) in the concentrate of the RO system. LSI is used for solutions up to 5000 ppm TDS; SDSI is used for high-salinity waters. Sulfate scaling potentials can be estimated by calculating the ratio of solubility products in the concentrate of the RO system to equilibrium values.

Scaling indexes are discussed in chapter 1. Readily available computer programs can be used to calculate LSI and SDSI values as well as saturation ratios based on equilibrium constants.

Pretreatment techniques to minimize scale include softening or demineralization to remove hardness and acid to remove alkalinity. Hydrochloric acid is preferred over sulfuric acid for acidification due to the enhanced risk of sulfate scale when using sulfuric acid. If the use of hydrochloric acid is not feasible, softening can be used to minimize the risk of sulfate scale. Operating conditions that will reduce the potential for silica scaling include higher feedwater temperature, high pH (within membrane tolerances), and lower RO recovery.

10.4 CHEMICAL TREATMENT IN RO SYSTEMS

Reverse osmosis systems provide substantial opportunities for chemical treatment. The RO feedwater must be carefully prepared to minimize suspended solids, scaling ions, free halogen residuals and microbiological contamination. The prepared feedwater should then be chemically treated to help prevent mineral scaling, plugging and microbiological degradation of the membranes. Finally, the reject water may require treatment for disposal.

10.4.1 Pretreatment Summary

Proper pretreatment of the feedwater to an RO system is critical for maintaining optimum performance and maximizing membrane lifetime. The specific objectives of pretreatment are to minimize or prevent the following:

- Fouling by suspended solids, organics, microbiological material, and colloids
- Scaling by $BaSO_4$, $SrSO_4$, $CaSO_4$, $CaCO_3$, and reactive silica
- Membrane degradation via exposure to high temperature, bacteria, oxidizing biocides (TFC membranes), and hydrolysis at high or low pH (CA membranes)

Table 2-23 lists feedwater quality requirements for CA and TFC membranes, and pretreatment techniques used to achieve this water quality.

TABLE 2-23
RO Feedwater Quality Requirements and Pretreatment Techniques

Item	Test	Value	Pretreatment
Foulants			
Solids	SDI	<5	Clarification, multimedia filtration, NaZ softening
	Turbidity	<1	coagulants
Iron, ppm	Analysis	<0.05	Oxidation ($KmnO_4$, H_2O_2, Cl_2), aeration, pH
Manganese, ppm	Analysis	<0.05	Filtration (greensand)
Organics, ppm	TOC	10-15	Chlorine, activated carbon, nanofiltration
Micro-organisms	Plate counts	Not specified[a]	Chlorine, biocides, filtration
Scalants			
Calcium carbonate	LSI (Concentrate)	<1	Softening, sequestrants, antiscalants
Barium, ppm	Analysis	<0.05[b]	PH
Strontium, ppm	Analysis	<0.1	
Silica, ppm	Analysis (Concentrate)	50-160[c]	Strong base ion exchange
Temperature			Heat exchange
CA membranes		35-95°F(1-35°C)	
TFC membranes		35-113°F(1-45°C)	
pH			Acid, caustic
CA membranes		4-6	
TFC membranes		2-11	
Chlorine, free, ppm	Photometric		Metabisulfite
CA membranes		1.0	
TFC membranes		0	

Notes:

a. Not specified by membrane manufacturers; keep counts as low as possible to prevent severe fouling.

b. Strongly dependent on pH, system recovery, and calcium and sulfate loading of feedwater. Under certain conditions, the maximum feedwater concentration of barium may be as low as 0.001 ppm to prevent barium sulfate scale.

c. Strongly dependent on pH, temperature, and system recovery.

10.4.2 Microbiocides

Only oxidizing biocides should be used in potable water RO systems. Sodium hypochlorite is most often used. Chlorine dioxide is effective and is less reactive to TFC membranes. A low level oxidizing residual should be maintained through the entire pretreatment train, to prevent buildup of biological deposits that could damage the membranes.

Dechlorination is required before the feedwater enters the RO units. As explained above, sodium metabisulfite is the reducing agent of choice in this case because it is soluble, reacts quickly and forms no harmful byproducts. The small amount of sulfate formed in the dechlorination reaction is usually not significant. Activated carbon is not recommended in this application because the carbon beds tend to become microbiologically contaminated.

10.4.3 Mineral Scale Control

Depending on the feedwater chemistry, it may be cost-effective to feed polymeric scale control chemicals to help prevent calcium carbonate, calcium phosphate, calcium sulfate, barium sulfate and silica scales from forming. Polymers are designed specifically to control each of these scales. Study the water chemistry, analyze deposits and select the appropriate products. Polymeric scale control chemicals are discussed in chapter 4.

10.4.4 Cleaning Chemicals

In spite of all pretreatment and chemical treatment efforts, RO membranes do gradually foul and therefore require periodic chemical cleaning. Both acidic and basic cleaning chemicals can be used, depending on the composition of the deposits and the sensitivity of the membrane (see section 10.5, below.)

10.5 MONITORING AND MAINTENANCE

The purposes for monitoring an RO system are:

- To ensure that the system is operating within design limits and to trigger needed responses to out-of-spec data.
- To determine if gradual fouling, scaling, or membrane degradation is occurring by observing system performance over time.

Note that all membranes experience "aging" even under ideal operating conditions. A sharp initial drop in productivity, as much as 5% in the first 10 days and a total of 12% in the first year, should be expected. However, membrane productivity should not decrease significantly after the first year. Expect only an additional 1% decrease between the first and third year of operation. Performance losses greater than this rate indicate that irreversible fouling or membrane degradation has occurred.

10.5.1 Monitoring Data

Table 2-24 lists the data that should be monitored routinely to evaluate how an RO system is performing.

(b) Table 2-24

(c) RO Performance Data Monitoring Form

Parameter	RO Inlet	RO Interstage	RO concentrate	RO permeate	Other
Pressure	X	X	X	X	Across each prefilter
Flow rate	X	X	X	X	
Conductivity	X	X	X	X	
Temperature	X		X		
PH	X		X		
SDi	X				Inlet and outlet to each multimedia filter
Chlorine, free	X		X		
Turbidity	X				
LSI			X		
MB plates (one/week)	X		X	X	Before/after each piece of upstream equipment

Ideally, data should be recorded at least once per shift, except the MB plate counts, which may be taken weekly. At a minimum, the data should be recorded at least once per day.

Basic RO systems are usually equipped with gauges or computer monitoring programs for pressure, flow rate, and conductivity of the feed, permeate, and concentrate streams. Some, but not all, systems include equipment for monitoring interstage conditions. Interstage data are important because some types of fouling and scaling affect only specific stages of an RO system.

Productivity, or "water flux", in the absence of fouling will decrease with time. The rate of this decline is a function of the membrane type and the operating temperature. Salt passage will normally increase with time and is a function of the membrane type, operating temperature, pressure, pH, and average feed concentration. Differential pressure or "pressure drop' through an element should <u>not</u> change with time, providing the feed and concentrate flow rate are held constant.

10.5.2 Normalization

Normalization of data is used to track and trend RO system performance – rejection, water flux, and pressure drop. Observed rejection and water flux are affected by several factors including temperature, pressure, recovery rate, and water chemistry as well as fouling, scaling, membrane degradation, and aging. To determine effects of fouling, scaling, and degradation only, raw operating data are converted or "normalized" to a standard set of conditions, thereby eliminating effects of day-to-day variations in temperature, pressure, and similar factors.

Note that differential pressure is affected by fouling, scaling, and membrane degradation only and does not need to be normalized. By monitoring differential pressure and normalized water flux and rejection over time, one can observe how the system is performing and can determine when a system should be cleaned.

<u>If raw data are used without normalizing, the true condition of the system will not be observed. The use of raw data could lead to improper recommendations and reduced membrane life.</u>

Most membrane manufacturers supply normalization programs to end users with the installation of the RO system, via the original equipment manufacturer (OEM). Where available, these programs should be used for monitoring the RO system. Refer to ASTM D 4516-85 for details on normalization.

10.5.3 Maintenance and Cleaning

Membrane cleaning schedules should be determined by the normalized system performance data and <u>not</u> by any predetermined schedule. Cleaning should be performed when any of the following occur:

- Normalized product flow has decreased by 10%
- The pressure-drop coefficient has increased by 10%
- The actual pressure drop across a stage reaches 50 psi

Failure to clean under these conditions may result in physical damage and permanent fouling of the membranes. Cleaning on a predetermined timetable or schedule is generally not acceptable because cleanings are either too frequent, which contributes to membrane degradation, or too late, after fouling or scaling has settled and become irreversible.

In rare cases, cleaning may be based on product quality. If quality becomes unacceptably low and there is no change in product flow or pressure drop, module seals should be inspected. Cleaning should be performed if the module seals show no damage.

Two types of cleaners are used separately for RO cleaning. A low pH cleaner is used to remove scale and metal oxides, and a high pH cleaner (or neutral for CA membranes) is used to remove organics, microbiological fouling, and silica. These cleanings can be followed with a biocide rinse.

Cleaning techniques vary from system to system, depending on the type and severity of fouling and the membrane type.

Many RO systems are delivered with a cleaning skid. This skid includes a tank, a cartridge filter, tank heater, and pump. All equipment should be sized such that a flow of 40 gpm *per tube* for 8-in. diameter modules can be maintained. Recirculation should be under just enough pressure to achieve the desired recirculation rate, but always less than 60 psi. Cleaning is most effective at high temperatures (typically 90 – 110° F) depending on the type of membrane.

RO systems should be cleaned off-line, one stage at a time. Fresh solution should be prepared using RO permeate quality water or better for each stage. Samples of fresh and used cleaning solution can be collected and analyzed for specific foulants and scalants removed from the membranes. Skid cartridge filters should be replaced after each stage is cleaned. These filters can also be analyzed for specific foulants and scalants removed from the membranes.

10.5.4 Storage and Layup

RO systems achieve optimum performance when they are operated continuously. However, there are circumstances when on-off operation or extended periods of downtime are required. Membranes must be carefully maintained when off-line to prevent microbiological fouling.

Each membrane manufacturer specifies specific membrane lay-up procedures. These procedures should be followed carefully to protect equipment warranties. Steps generally involve cleaning and flushing, using chlorine, bisulfite solution and permeate water.

10.6 TROUBLESHOOTING

The first step in troubleshooting RO systems is to identify the type of problem.

- Operational problems are caused by malfunction of equipment, such as pumps, valving, probes, or gauges. These problems can be identified and remedied by testing and servicing or replacing defective equipment.
- Performance problems are caused by fouling, scaling, and membrane degradation. These problems are manifested by changes in differential pressure, salt rejection, and normalized water flux.

While operational problems are relatively easy to identify and remedy, the causes of performance problems require more in-depth investigation.

Table 2-25 lists some of the most common causes of performance problems.

Table 2-26 lists symptoms of common performance problems.

TABLE 2-25

Common RO System Performance and Operating Problems

Performance problems:

- Changes in feedwater quality and temperature
- pH change (CA membranes)
- Poor pretreatment
- Poor maintenance of pretreatment
- Operational problems of system

Operational problems:

- Higher recovery than design
- Higher/lower operating pressure vs. design
- Improper storage
- Flush of off-line membranes with RO feedwater rather than RO permeate water

TABLE 2-26

RO Troubleshooting Guide

Problem	Product Flow	Salt Passage	Pressure Drop	Location
Scaling	Decreased	Increased	Increased	Last stage
MB Fouling	Decreased	Normal/increased	Normal/increased	Any stage
Colloidal Fouling	Decreased	Normal/increased	Normal/increased	First stage
Degeneration	Increased	Increased	Decreased	First stage
Abrasion	Increased	Increased	Decreased	First stage

11.0 Electrodeionization

11.1 INTRODUCTION

Continuous Electrodeionization (EDI) is a membrane/resin deionization process that is used in the production of very high purity waters. EDI was first developed more than 40 years ago as a chemical-free process, primarily for laboratory work. Recent developments in EDI have made the elimination of regeneration chemicals a practical reality and the process has been recently used in larger commercial applications. Figure 2-21 shows a modern stacked array of EDI cells in a commercial unit.

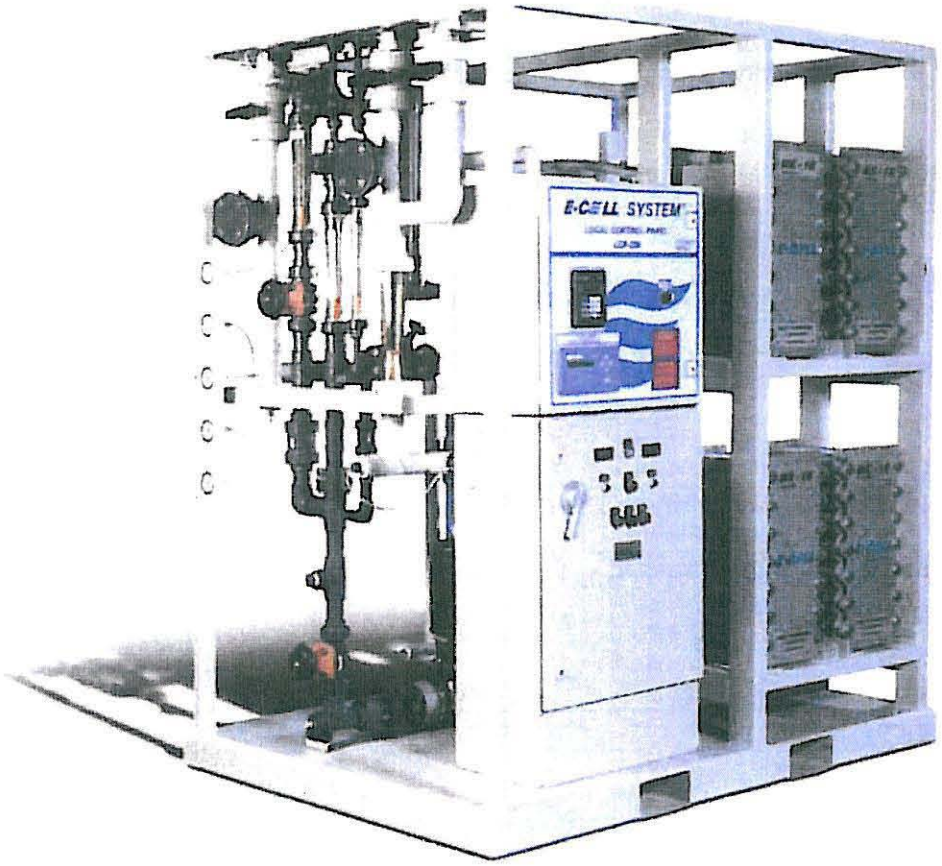


FIGURE 2-21
A commercial electrodeionization unit.

11.2 PRINCIPLES OF ELECTRODEIONIZATION

Electrodialysis (EDI) employs direct current electrical power as the energy source for deionization. Ions in solution are attracted towards electrodes with the opposite electrical charge. By dividing the space between the electrodes into compartments with cation and anion selective membranes, salts can be removed from half the compartments and concentrated in the remaining compartments. With provision for feeding and taking away from these sections, a continuous desalination process is established. The membranes used in continuous electrodeionization can be ion exchange resins cast in sheet form and usually reinforced with a backing cloth imbedded in the sheet.

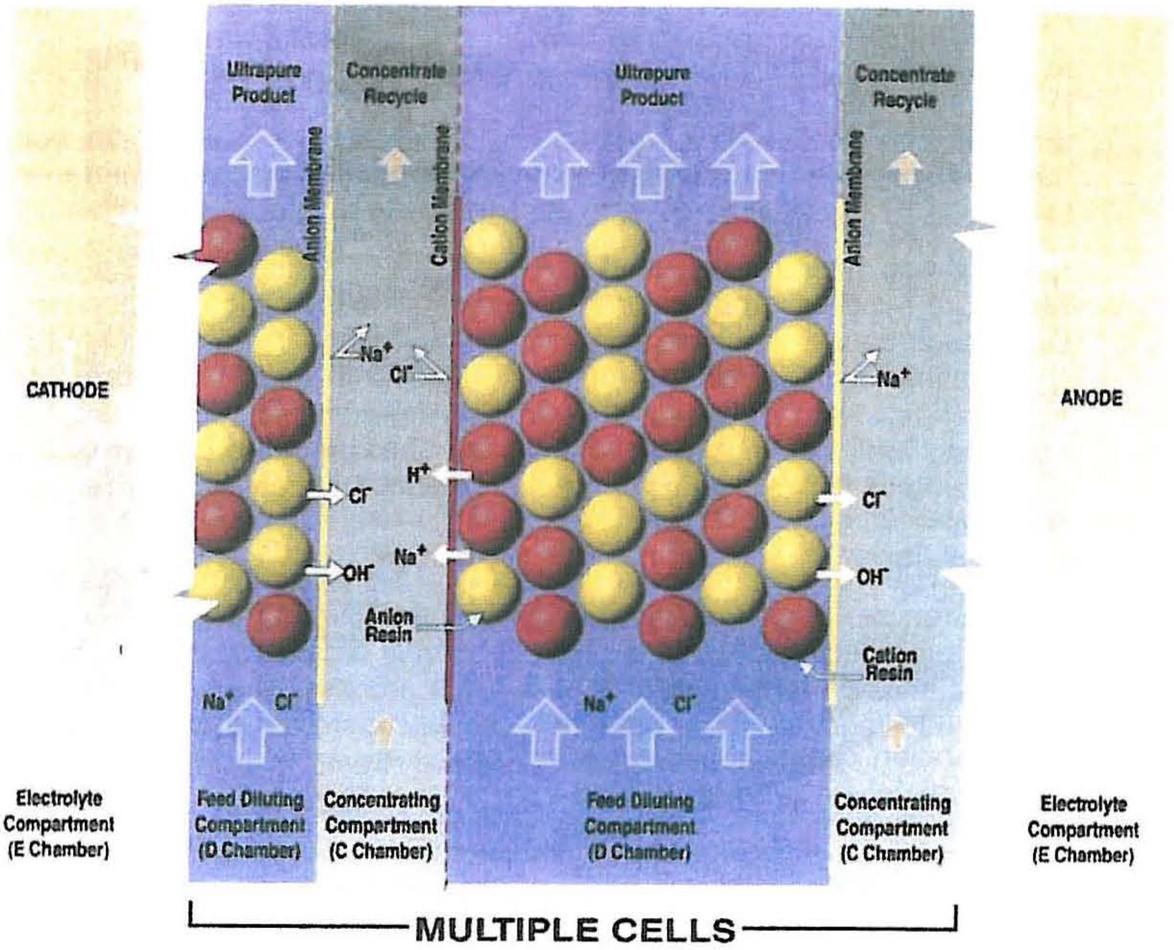


Figure 2-22
Drawing of an electrodeionization membrane cell.

A typical EDI stack is made up of a number of dual-chambered cells sandwiched between two electrodes (see Figure 2-22). Ion-exchange resin is located between two membranes which make up one of the cell pair: a cation membrane, specifically designed to allow migration of only cations, and an anion membrane, which allows the migration of only anions. This is the D Chamber in Figure 2-22. The resin bed is continuously regenerated by a DC current applied across the cell. When contaminant ions such as sodium and chloride are present in the feedwater, they undergo the usual ion-exchange reactions in which they attach to their respective ion-exchange resins, displacing hydrogen and hydroxide ions as in conventional mixed-bed ion-exchange.

Once adsorbed on the ion-exchange resin, the contaminant ions move through the resin from bead to bead, until they permeate the membranes and enter the adjacent concentrate stream, the C chambers. Sometimes salt (NaCl) is added to the concentrate loop to improve current efficiency and reduce the amperage needed for continuous regeneration. This concentrate stream of contaminant ions is then swept out of the stack.

In a typical EDI system, 90-95 percent of the feed water is directed through the D chamber while 5-10 percent is diverted through the C Chambers. Ions are removed from the stack by bleeding off a percentage of the water from the "concentrated loop". This water, with a pH typically in the range of 5 to 8, can be recovered and directed back to the inlet of the RO system.

In the diluted compartment of an EDI stack, mixed cation-and anion-exchange resins are sandwiched between anion and cation exchange membranes. The DC voltage causes the hydrogen and hydroxide ions in water to transfer from the diluting compartment, through the resin, toward their corresponding membranes. As they pass through the membranes, the hydrogen and hydroxide ions recombine to yield water. This production and migration of hydrogen and hydroxide ions is the mechanism that continuously regenerates the resin.

The EDI reject stream (the brine) is usually of higher purity than the water from the pretreatment system. As a result, the reject stream can be fed back into the system directly ahead of the RO, effectively eliminating a waste stream. In contrast, mixed-bed regeneration is a batch process, and because chemicals are used to regenerate the resin bed, the waste stream contains three to four times the ionic waste of the typical EDI waste stream.

EDI's most important advantage is that no chemicals are required for regeneration. Therefore, no bulk storage or neutralization tanks for regeneration chemicals are needed, and storage, handling, and disposal of hazardous chemicals are reduced.

12.0 Glossary of External Treatment Technology

12.1 REVERSE OSMOSIS SYSTEM DESIGN TERMS

Reverse osmosis systems are designed using many membrane modules in series/parallel arrangements. Terms used to describe membrane systems are defined below:

Array: Arrangement of tubes. Array describes the number of stages and number of tubes in each stage.

Module: Smallest unit that actually contains the membrane.

Pass: Trains in series. Product from one train becomes feed to another train. The product water from second pass is very low in dissolved solids.

Stage: Two or more tubes in parallel. The maximum recovery from a single stage is about 50%, hence stages are placed in series to increase the recovery from the overall system.

Train: Entire set of modules, tubes, and stages.

Tube: Pressure vessel that contains several (typically 4-7) membrane modules in series.

12.2 ION EXCHANGE GLOSSARY

Acidity: An expression of the concentration of hydrogen ions present in a solution.

Absorption: The attachment of charged particles to the chemically active groups on the surface and in the pores of an ion exchanger.

Alkalinity: An expression of the total basic anions (hydroxyl groups) present in the solution.

Anion: A negatively charged ion.

Attrition: The loss of resin through abrasion in a resin bed, which results in physical breakdown of resin beads.

Backwash: Reverse flow of water through a resin bed (i.e., in at the bottom of the exchanged unit, out at the top) to clean and reclassify the bed after exhaustion.

Bed: The ion exchange resin contained in a column.

Bed Depth: The height of the resinous material in the column.

Bed Expansion: Increase in bed depth due to backwashing and/or regeneration.

Bicarbonate Alkalinity: The presence in a solution of hydroxyl (OH-) ions resulting from the hydrolysis of carbonates or bicarbonates. When these salts react with water, a strong base and a weak acid are produced, and the solution is alkaline.

Capacity: The adsorption ability possessed in varying degree by ion exchange materials. Usually expressed as grains per cubic foot.

Cation: A positively charged ion.

Channeling: "Short circuiting" through the bed due to faulty operational procedures, in which the solution being treated follows the path of least resistance, runs through furrows, and fails to contact active groups in other parts of the bed.

Cycle: A complete course of ion exchange operation; from backwash through brining rinsing and back to operation.

Deionization: A general term meaning the removal of all charged ions from solution.

Demineralization: Synonymous with deionization.

Efficiency: The effectiveness of operational performance of an ion exchanger compared with design. Efficiency in the adsorption of ions is expressed as the quantity of regenerant required to effect the removal of a specified unit weight of adsorbed material, e.g., pounds of salt per kilograin of dissolved solids removed.

Effluent: The solution which emerges from an ion exchange column.

Elution: The stripping of adsorbed ions from an ion exchange material by the use of solutions containing other ions in relatively high concentrations.

Exhaustion: The state in which the resin is no longer capable of useful ion exchange; the depletion of the exchanger's supply of available ions. The exhaustion point is determined arbitrarily in terms of: (a) a value in parts per million of leakage; (b) the reduction in quality of the effluent water determined by some test parameter such as conductivity.

Flow rate: The volume of solution passing through a certain quantity of resin within a given time. Usually expressed in terms of gallons per minute per cubic foot of resin, or as gallons per minute per square foot of bed area.

Freeboard: The space provided above the resin bed in an ion exchange column to allow for expansion of the bed during backwashing.

Grain: A unit of weight; 0.0648 grams.

Grains per gallon: An expression of concentration of material in solution, generally in terms of calcium carbonate. One grain (as calcium carbonate) per gallon is equivalent to 17.1 parts per million.

Hardness: The sum of calcium and magnesium ions in the water, expressed as calcium carbonate.

Hydrogen cycle: A complete course of cation exchange operation in which the active regenerant used is hydrogen based, such as sulfuric acid.

Hydroxide: The term used to describe the anionic radical (OH-).

Influent: The solution which enters an ion exchange unit.

Ion: Any dissolved charged particle in solution.

Leakage: The level of influent ions that are not absorbed or exchanged and appear in the effluent.

Negative charge: The electrical potential which an atom acquires when it gains one or more electrons; a characteristic of an anion.

pH: An expression of the acidity of a solution; the negative logarithm of the hydrogen ion concentration (pH 1, very acidic; pH 14, very basic, pH 7, neutral at ambient temperature.)

Positive charge: The electrical potential acquired by an atom which has lost one or more electrons; a characteristic of a cation.

Raw water: Untreated water from wells or surface sources.

Regenerant: The solution used to restore the activity of an ion exchange. Acids are employed to restore a cation exchanger to its hydrogen form; brine solutions may be used to convert the cation exchanger to the sodium form.

Regeneration: Restoration of the activity of an ion exchanger by replacing the s adsorbed from the treated solution by ions that were adsorbed initially on the resin.

Rinse: The operation which follows regeneration; a flushing out of excess regenerant solution.

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CHAPTER 2
TRAINING QUESTIONS

1. In your own words, explain why pretreatment of incoming water is critical to the success of many water treatment programs. (Introduction, section 2.2, and chapter 2, section 1.0).
2. Consider the process of aeration. What is aeration and what is it used for? Describe the three separate steps by which aeration works (sections 2.1 and 2.2).
3. A system is installed to remove carbon dioxide from boiler feed water. The pH is 6.5 and there is a need to remove more carbon dioxide. What would you do? (section 2.4.2 and Figure 2-1).
4. Consider clarification. What is the purpose of clarification and what are the three processes by which clarification is achieved? What chemicals are used in these processes? (Sections 3.1 and 3.2, and Table 2-1).
5. What is the purpose of jar testing and how is it done? (Section 3.2.4).
6. A sludge blanket clarifier is experiencing floc carryover, and turbidity is higher than desired. What steps should you take to troubleshoot the system (see Chapter 2, section 3)?
7. What is precipitation or lime softening? Explain how lime (calcium oxide) or quicklime (calcium hydroxide) can be used to remove calcium and magnesium hardness from a water supply. When is soda ash used? (Sections 4.1 and 4.2, plus chapter 1 sections 6.3 and 6.4).
8. Given the following water analysis (all as CaCO3), what will the analysis be after addition of lime and soda ash in an ambient temperature lime softening process? Calculate the amounts of lime and soda ash required to soften this water. (Section 4.2.4, and chapter 1 section 6.4.4).

Total hardness:	250 mg/L
Calcium hardness:	150 mg/L
M alkalinity:	150 mg/L
pH:	7.5

9. What is filtration used for and what are the three basic filtration mechanisms? What are the advantages of mixed media filtration systems? Where are bag and cartridge filters used and what are the advantages and disadvantages compared with sand filters? What is the expected effluent turbidity from a sand filter? (Section 5.0).
10. In ion exchange systems, what does selectivity for various ions mean? (Sections 6.1 and 6.2, and Table 2-5).
11. List the four basic types of water treatment resins and explain the advantages and disadvantages of each type.

12. A gel strong base anion resin analysis shows a TOC throw of 300 ppm, 16% broken beads, a density of 46 and a salt splitting capacity of 22. What would you recommend? What effect do you think the condition of this resin, if left in the system, would have on water quality? (Sections 6.7 and 6.8).
13. What are the four major steps in sodium zeolite softening? What are the flow rates for each step (see section 7.3)?
14. A sodium zeolite system is experiencing continuing short runs. Describe what an elution study is and what might be causing the short runs. (Sections 7.4 and 7.5, Table 2-12 and Figure 2-15).
15. What is demineralization? Describe the purpose of each step in a simple demineralization system consisting of a strong acid cation (SAC) unit, a decarbonator, and a strong base anion (SBA) unit. What tests are run at each stage for monitoring? (Section 8 and Table 2-14).
16. A demineralizer system is experiencing short runs. Monitoring has indicated premature silica breakthrough. What are the most likely causes of the problem and what actions should be taken? Section 8.7 and Table 2-15).
17. What is the purpose of condensate polishing? List five types of polishers. (Section 5.6, section 9 and Table 2-19).
18. What is the purpose of reverse osmosis? Describe how reverse osmosis works. Define percent recovery and percent rejection. (Section 10.0).
19. How are RO systems monitored for feedwater quality requirements? What are the critical tests to minimize membrane fouling? (Section 10.5 and Tables 2-22 and 2-23).
20. What is normalization and why is it important in monitoring an RO system? (Section 10.5).
21. Compare ion exchange with reverse osmosis. When is it more economical to use RO? (section 10).
22. What are the benefits of using RO first, followed by demineralization, in the same system (sections 8 and10)?
23. What is electrodeionization (EDI) and where is it used? (Section 11.0).
24. What pretreatment system would be recommended for the following applications? in your answers, consider all the concepts in chapter 2 plus the ASME boiler operating guidelines in chapter 3, Table 3-13.
    a. A 100 psig boiler system used for steam heating. Make-up city water is high in hardness. Some condensate is returned to the system.
    b. A 900 psig boiler system used for process steam, heating steam and to drive a steam turbine used for power generation. Make-up is city water high in hardness, silica and alkalinity.

c. A plant will use river water for make-up to cooling towers used for cooling water in process applications and some HVAC. The same river water will be used for boiler system make-up for 400 psig boilers used for heating and some steam driven pump applications. The river water is high in TOC and suspended solids, and moderately high in hardness and alkalinity.

ANSWERS TO CHAPTER 2 TRAINING QUESTIONS

Answer to Question 1

In many cases, the quality of available incoming water supplies is not suitable for the required applications. Without pretreatment, chemical treatment would either be too costly or ineffective. Good pretreatment can save costs, increase reliability and reduce downtime.

From a business standpoint, effective external treatment knowledge helps to establish you as the water treatment expert and can help stabilize and gain business. Significant cost savings can result for the customer or prospect. Also, some pretreatment processes include chemical applications, such as ion exchange resin cleaners and reverse osmosis dispersants to minimize the potential for fouling of membranes.

Answer to Question 2

Aeration is a mechanical process for providing intimate contact of air with water to remove certain gases and metals. Aeration proceeds in three separate steps:

1. Intimate contact of air with water.
2. Gas molecules pass across the air-water phase.
3. Depending on the goal, a level of equilibrium is reached.

Answer to Question 3

In the process of de-gassing solutions containing carbon dioxide, a lower pH will remove more CO_2, so addition of acid to lower the pH to 5.0 will effectively remove almost all of the CO_2.

Answer to Question 4

The purpose of clarification is to remove suspended solids, turbidity, organic matter and color from make up water. The three clarification processes are: coagulation, flocculation and sedimentation. Various chemicals are used, depending on the process requirements. Aluminum and iron salts are common, together with organic polyelectrolytes.

Answer to Question 5

Jar testing is used in the field to evaluate clarification chemicals and develop programs for site-specific applications. The test consists of adding chemicals to beakers containing the water to be treated, and mixing them using carefully controlled procedures. Products are evaluated by observing the rate of settling, the consistency of the sludge and the clarity of the supernatant water.

Answer to Question 6

Many factors influence clarifier performance, such as temperature changes, chemical addition, pH, rake speed and slurry settled volume. Sludge blanket clarifiers can be sensitive to chemical treatment, temperature, throughput rate and other factors. Floc carryover can be due to a number of factors; some of the most common include flow surges, thermal changes and improper chemical feed. Check the sludge bed level. Sometimes adjustment of the sludge bed to a lower level while maintaining the proper sludge concentration will solve the problem. Jar testing is the principle tool used for field evaluation of clarification processes.

Answer to Question 7

Precipitation softening refers to the removal of calcium and magnesium hardness from water by precipitation as the respective carbonate salts. Lime and quicklime react with bicarbonate alkalinity in the water to make carbonate alkalinity. Carbonate reacts with an equivalent amount of hardness (temporary hardness) in the water, plus the hardness added as lime, to precipitate calcium carbonate. Lime also precipitates magnesium as magnesium hydroxide. Soda ash (sodium carbonate) is added to provide additional carbonate alkalinity to precipitate the remaining permanent calcium hardness in the water. For extra credit: Can you write and explain the equations for these reactions? See sections 4.2.1 and 4.2.2.

Answer to Question 8

The resultant water analysis (all expressed as ppm CaCO3) will be:

	Raw Water	Treated Water
Total Hardness	250	81
Calcium Hardness	150	35
Magnesium Hardness	100	46
"P" Alkalinity	0	37
"M" Alkalinity	150	55

Amounts of lime and soda ash required will be:

Lime:	250 mg/L
Soda ash:	100 mg/L

Answer to Question 9

Filtration is used to separate suspended and colloidal impurities from water by passage through a granular bed of compound media. The three mechanisms are: transport through the media, attachment to the surface and movement of filtered particles deeper into the media.

The advantages of mixed media filters are deeper bed penetration and longer filter runs. Bag and cartridge filters are used in smaller systems where backwashing is not practical and for ease of operation. Disadvantages are manpower required to replace the bags or cartridges, and costs involved.

The expected effluent turbidity from a properly operated sand filter should be <1 JTU.

Answer to Question 10

Selectivity is the preference of a particular resin for one ion over another. For example, a cation (sulfonic acid) resin will first remove calcium, then magnesium and finally sodium. This explains why sodium chloride is effective as a regenerant, since it is easily displaced on the bead by other cations. The selectivity is overcome during regeneration by high concentrations in the regenerant solution.

Answer to Question 11

The four basic types of resins are:

- Strong Cation or Strong Acid: Removes all cations, less sensitivity to flow rate and temperature. Low capacity and poor regeneration efficiency.
- Weak Cation or Weak Acid: High capacity and regenerative efficiency. Will not remove permanent hardness, sensitive to temperature and flow.
- Strong Anion or Strong Base: Best silica and carbon dioxide removal, lower capacity and poor regenerative efficiency.
- Weak Anion or Weak Base: Good capacity and regenerative efficiency, no silica or carbon dioxide removal, poor resin stability.

Answer to Question 12

The TOC of 300 ppm indicates organic fouling. Broken beads over 15% can be an indication of degradation. The density and salt splitting capacity indicate the resin may be fouled or degraded. Check quality of effluent and run lengths. Also check for leakage from the cation and quality of the caustic regenerant. At a minimum, the resin should be cleaned and replacement should be considered. Short runs and reduction in quality of the effluent may be affected. Salt splitting capacity is an indication of the ability of the resin to remove weakly ionized anions, such as SiO2. Check for silica breakthrough.

Answer to Question 13

The four major steps and flow rates are as follows:

STEP	FLOW RATE
• Service	6 to 8 GPM/ft^2
• Backwash	5 to 6 GPM/ft^2
• Regeneration	0.5 to 1 GPM/ft^2 of 10% brine solution for approximately 30 minutes.
• Rinsing	Slow rinse or displacement at a volume of 10 gallons per cubic feet of resin at same flow rate as regeneration. Follow with a fast rinse of 1.5 to 2.0 GPM/ft^3

Answer to Question 14

An elution study plots the concentration (specific gravity) of brine from a zeolite softener during a regeneration, using a hydrometer and graduated cylinder. Given the capacity of any resin with a given brine concentration (available from the resin manufacturer data), the system's actual capacity can be determined.

Short runs are often caused by poor regeneration procedures and can be solved by adjustment of flow rates and brine contact time. Resin fouling and loss of resin are other frequent causes of short runs. Opening the vessel for inspection prior to regeneration, as well as after, can indicate if channeling is occurring or if a mechanical problem exists. The elution study may indicate low salt concentration or regenerant channeling.

Answer to Question 15

Demineralization is a process for removing all cations and anions from a water system. It is generally applied to higher pressure boiler systems or for process use. A strong acid cation unit in the hydrogen form changes all cations to the hydrogen form. The decarbonator removes carbon dioxide and reduces alkalinity. The strong base anion unit removes all remaining anions.

Demineralizer control tests should be run daily, preferably on each shift. Required tests are as follows:

SAC: pH and alkalinity.
Decarbonator: no tests generally run.
SBA: silica and conductivity.

Answer to Question 16

The most likely causes for silica breakthrough are organic fouling, resin degradation and poor regeneration. Actions that should be taken include inspection of the vessel to check for proper quality of resin, examination of the resin to check for fouling, check of the quality of caustic (some caustic supplies contain organics), resin analysis to determine TOC levels and review of regeneration practices.

Answer to Question 17

Condensate polishing is used to remove contaminants such as iron, copper, hardness and organic matter from condensate systems. Condensate polishing is site-specific, depending on the system design and the condensate composition. Types of condensate polisher systems include simple cartridge filters, magnetic filters, precoated filters, sodium zeolite resins and mixed bed resins.

Answer to Question 18

Reverse osmosis (RO) is an alternative process for demineralizing water. Reverse osmosis works by passing water under pressure through a semipermeable membrane that removes contaminants, which remain in the "concentrate", while pure water is produced in the "permeate".

Percent recovery is the product (permeate) flow divided by the feedwater flow.

Percent rejection is the difference between the concentration of salts in the feed water and the permeate or product water, divided by the concentration of salts in the feed water.

Answer to Question 19

RO inlet water should be monitored for conductivity, pH, SDI (silt density index), chlorine, turbidity, LSI and microbiological activity (total counts). Other parameters should be monitored at RO interstages, concentrate and permeate points.

Foulants that most often impact RO membranes include suspended solids, colloidal silica, iron oxides, organics and microbiological matter. Tests that can be used to measure for these contaminants include silt density index (SDI), turbidity, TOC, microbiological plate counts and elemental analyses for iron, silica and sometimes other elements.

Answer to Question 20

Normalization corrects RO performance information, such as flows of permeate, rejection water rate and other parameters, to a standard set of conditions. These parameters are affected by temperature, pressure, water chemistry and other operating factors. Most membrane manufacturers supply normalization programs. ASTM D4516-85 has details on normalization procedures.

Answer to Question 21

RO can economically treat water higher in total dissolved solids (400 to 3000 TDS). The permeate will usually have 5% of the TDS remaining in solution after RO treatment. This may not be adequate for higher pressure boilers. Ion exchange can economically treat water that is low to moderate in TDS, and TDS in the effluent can be 1% of incoming TDS. In addition, RO can eliminate the need to handle caustic and acid used for regeneration.

Answer to Question 22

The advantages of using both systems together include savings due to decreased regenerant use, extended resin life and run lengths, less organic fouling of the anion resin, improved water quality and lower labor and maintenance requirements. A typical 500 TDS water, treated by RO, would result in an effluent of about 25 TDS. Treated by ion exchange, the effluent would be approximately 10 ppm TDS. This same water treated first by RO followed by demineralization would have an effluent of about 1 ppm TDS. Organics and silica would also be very effectively controlled. Each system is different and each has to be evaluated separately. Many equipment manufacturers, as well as membrane and resin manufacturers, have computer programs that can be used for this purpose.

Answer to Question 23

EDI is a membrane/resin deionization process used for the production of high purity water. The process uses direct current electrical power as the energy source for desalting. Ions in solution are attracted towards electrodes with the opposite electrical charge. Different compartments consist of cation and anion resins cast in sheet form similar to membranes.

Answer to Question 24

a. Generally a sodium zeolite softener will suffice for low pressure boiler makeup water pretreatment.

b. Demineralized water will be required for this system, particularly since steam turbines require high purity steam. The equipment could be a resin based demineralizer, an RO system, or even EDI. Process water uses should always be checked for water quality requirements.

c. Pretreatment to remove TOC and suspended solids will require clarification followed by filtration. In line filtration could also be considered. Chlorination of the make-up water will also be required. For the boiler system, sodium zeolite softening may suffice, but demineralization would be a better choice.

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Promoting a favorable environment for the water treatment industry

Technical Reference and Training Manual

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CHAPTER 3

Boiler Systems

Table of Contents

1.0 Overview

Steam was one of the foundations of the Industrial Revolution. After water and wind power, it was the next important step in the process of industrialization. Unlike water or wind power, steam could be generated at will and in the desired location. But the main drawback was that its generation and handling required highly specialized technology. Among these were the ability to provide energy in a concentrated form, develop equipment capable of withstanding the temperatures and pressures involved, and finally of providing water of sufficient quality to prevent failure of the equipment due to corrosion and fouling.

This chapter deals primarily with the last issue, water quality and treatment. Regardless of the boiler design and the uses of the steam, the basic principles of steam generation remain the same. Sections 3.0 to 3.3 cover boiler design and steam generation. These sections are not intended to be exhaustive, but merely illustrative. The purpose of including those sections is so that the reader will be familiar with the equipment and their principles of operation. In that way, there will be a better understanding of how water treatment relates to these systems, and how to recognize problems and deal with them effectively.

The remaining sections in chapter 3 address the specifics of water treatment and related troubleshooting issues. Study of these sections should provide the reader with a reasonably thorough understanding of how to treat specific systems, and to assist end users in operating their boiler systems properly. Providing boiler feed water of the correct quality for various types of boilers and many different uses of steam is covered in chapter 2 (external treatment, or pretreatment).

The steam generation industry today covers a wide range of technology, from simple cast iron and firetube heating boilers to electric power generating stations operating at supercritical pressures above 3200 psi. This chapter covers this entire pressure range, in an effort to give the reader a useful understanding of the entire field of steam generation.

However, most readers will have specialized interests, in low, medium or high pressure boilers. With a great deal of overlap, these groupings correspond roughly to the HVAC market, general industrial uses of steam, and the electric utility business. Readers are therefore encouraged to browse this chapter, study the subjects most appropriate to their interests, and read selectively in more technical topics to broaden their knowledge and find specific information as needed.

As an aid to this process, sections 7.0 and 9.0 include summaries of material important in low and medium pressure boilers. Interested readers are encouraged to study these summaries and then read the more detailed information in each section.

2.0 Steam

Steam is the gaseous phase of water. Its properties are somewhat unique from most other vapors. The liquid phase exists at ambient temperatures and pressures. As pointed out in chapter 1, water has a very high heat capacity. The heat of vaporization also is high relative to most other liquids. This means that steam stores more latent energy than most other liquids on a molar or weight basis. As such it is a very efficient medium for the transfer of heat energy or mechanical energy. Fortunately for the world economy, water is also readily available and inexpensive. The main operating costs in boiler systems are the costs involved in purifying raw water sources to make boiler feed water (chapter 2) and the energy costs involved in converting water to steam.

2.1 USES OF STEAM

Industrial uses of steam include electrical and motive power, air heating, HVAC, sterilization, and process heating. Process heating may be by indirect contact in a heat exchanger, or by direct contact as in food preparation. This manual deals only with indirect contact uses.

The earliest uses of steam were for transportation, in trains and ships. Later, steam was used for direct powering of machines. Factories generated steam which drove turbines. These, in turn, drove shafts with belt or geared transmissions connected to power equipment. Today, modern steam turbines generate most of the world's electric power.

Next, steam was used for direct heating of buildings. Today, many large office and apartment buildings use steam heat. Steam is generated in small boilers or in large central plants and conveyed by steam lines throughout a city area. Later, steam was used to power air conditioning (HVAC) equipment. This can be either of the turbine (compressor mode) or absorption type (see chapter 4). This changed the way of life for office and factory workers, and permitted the design of modern, completely enclosed high rise buildings.

Steam is used in chemical plants to provide both indirect and direct heating of reactors and distillation towers. Modern chemical plants and refineries have numerous boilers, distributing steam at various pressures to distant locations for a variety of processes. The steam distribution and condensate recovery systems are highly complex, and require sophisticated knowledge and products in order to function.

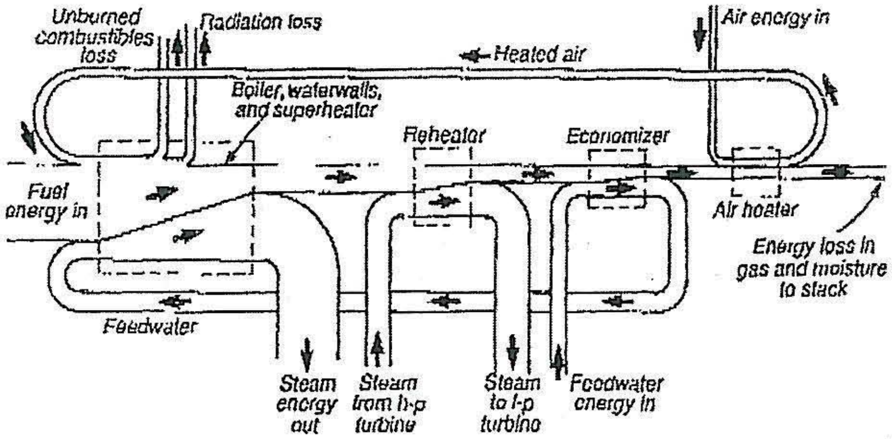
In the paper industry, directly injected steam is used to cook the wood chips in the pulping process. Steam is also used to heat the drying drums on the paper machines. In many cases, steam directly or indirectly contacts packaging materials for food or pharmaceuticals. That steam must meet rigid standards for health and safety, as its residues may be ingested. The various papermaking waste products (liquors) are concentrated by steam heating, and in some cases used for fuel in recovery boilers (black liquor recovery boilers).

Steam is used to humidify the air in office buildings, hospitals, electronics manufacturing plants and similar facilities that require a controlled humidity atmosphere. This can be done indirectly, by using a steam-heated heat exchanger to boil deionized water, or directly by injecting boiler steam into the air space. Another area of direct contact steam use is in the food processing industry. Cooking, sterilization, waste concentration and processing operations (feather removal in chicken processing and fat rendering in meat plants, for example) are all dependent on direct contact with steam.

Direct contact steam, and steam for food processing and pharmaceutical applications, is subject to many FDA regulations and standards for purity and toxicity. Direct contact steam purity is not covered in this manual. The regulations are constantly changing, so that any discussion or listing of specific regulations, products or treatment limits cannot be assumed to be correct in the future. It is best practice to consult the appropriate agencies or the Federal Register for up to date and accurate information (Section 11.0).

2.2 THE STEAM GENERATION CYCLE

The principle segments of the steam generation cycle are the feedwater preparation system, the boiler and steam generation system, and the condensate system. A typical cycle is shown schematically in figure 3-1.



Figurer 3-1. Schematic drawing of a typical steam generation cycle.

2.2.1 Makeup Water

Boiler makeup is raw water that has been pretreated as described in chapter 2 to make the quality suitable for use as boiler feedwater. Makeup water is required to replace lost condensate or process steam that is not returned to the system. Quality may range from raw city or well water to clarified and/or softened water to high purity demineralized water. Quality is dictated by the pressure range of the boiler and the end use of the steam.

Makeup water is technically part of the feedwater, but it is generally introduced separately into the boiler system. A separate feed line to the hotwell of a condenser, the condensate storage tank, the inlet to a deaerator, or the storage tank of a deaerator can be used for the introduction of makeup water. In some low pressure boilers, makeup water may be introduced directly into the steam drum.

Makeup water has not been deaerated or heated, and so represents a load on the heating, deaeration, and chemical feed requirements for the boiler. For that reason, it is important to limit the amount of makeup water, consistent with other operating requirements. For calculation purposes, makeup is treated as feedwater, but for operational purposes it is treated as a separate stream.

Boiler design is intended to accommodate the various technical challenges in producing steam. Some of these include the purity of the water (and keeping it pure), heat transfer to the water, minimizing corrosion, and containing the pressure of the steam. Other problems include steam quality and purity targets, pressure control, condensate treatment, and monitoring and control in general. Quality and purity targets are explained in the introduction to this manual.

2.2.2 Feed Water

Feed water is the water that is fed from the boiler feed pumps to the boilers. The composition can range from treated, deaerated condensate in high pressure boilers to untreated makeup water in many small, low pressure systems. Feed water may be heated in feedwater heaters, mechanically treated for oxygen removal, and chemically treated for residual oxygen removal and pH adjustment. Additionally, it may be passed through a condensate polisher. Usually, boiler treatment chemicals are not introduced into the feedwater, but they can be. If attemperation water (section 4.7) is extracted from the boiler feedwater, then only volatile chemicals should be fed to the feedwater.

2.2.3 Boiler Water

Boiler water is the water which is circulated in the boiler itself, the part of the system that is directly heated by the energy source. Examples of such energy sources are fossil fuel, waste fuels, nuclear fuel, sunlight, electric resistance heaters, or spent turbine gases. The water is heated to the boiling point at the pressure of the boiler, steam is separated from the water and directed to the system process, and the water is recirculated through the heat source. Usually a portion of the boiler water is removed via blowdown to maintain the correct chemical levels in the boiler, including the dissolved solids from the feedwater. Often, the only blowdown is from a sample line. Sometimes blowdown is directed to a flash tank where the residual heat is recovered.

2.2.4 Steam

Steam is the vapor phase of the water from the boiler. It is the working fluid for the process in use, and some of it may be used for feedwater preheating and deaeration. It may be saturated or superheated. Chemicals may be added to the steam for pH and corrosion control in the condensate system. See section 5.3.5.

2.2.5 Condensate

Condensate is steam that has been cooled to below its dew point (the saturation temperature at the partial pressure of the steam). It is collected and sent to a condensate storage tank (or condenser hotwell) from which it is fed to the feedwater train via the condensate feed pumps. In some systems, the condensate is either discarded or used in some other process. In those systems the feedwater is composed solely of makeup water.

3.0 Boiler Designs

Boilers are mechanical devices for generating steam from liquid water by the application of heat. The term boiler implies a direct transfer of heat to the water from the energy source. The energy source can be combustion of fossil fuels, electrical heaters, or nuclear fission. Boilers are differentiated from steam generators in that the latter generate steam indirectly from the transfer of heat to the water via a heat transfer medium. No fuel is burned in a steam generating system. The heat transfer medium may be a molten metal, for example, or pressurized water. Steam generators are common in industrial plants and some types of nuclear power stations.

Because of the differences in heat transfer methods, the design of boilers is different from that of steam generators. Boilers have a high-pressure differential across the tubes, and so require heavy gauge tubing. Steam generators usually have a low-pressure differential, and so function more like heat exchangers. The tubing is generally thin walled.

Both types of systems can have smooth bore or rifled bore tubing. The latter, known as enhanced tubing, provides for more turbulent water flow, therefore better heat transfer.

This chapter deals with boilers rather than steam generators unless otherwise stated.

3.1 WATER TUBE and FIRE TUBE BOILERS

Water tube boilers have the water flowing inside the boiler tubes, and the hot gases impinge on the outside surface of the tube. In fire tube boilers, the reverse is true. For a given steaming rate (pounds per hour), the water velocity in a water tube boiler will be higher. This provides for better mixing, heat transfer, and lower fouling potential. Operating pressures range from ambient to over 3000 PSIG.

Firetube boilers are typically smaller and less expensive than equivalent pressure and load watertube boilers. They are often referred to as firebox boilers. These boilers handle load changes better than watertube boilers. They are very rugged, much less prone to failure, and easier to operate than water tube boilers. Firetube boilers cannot produce superheated steam. Most are limited to about 40,000 pounds of saturated steam per hour.

Most large industrial boilers are of the watertube type. These may be package type, with an upper operating load of about 250,000 pounds per hour of saturated steam, or they may be field-erected (as in power boilers), with steam loads of up to several million pounds per hour. Operating pressures can be as high as 2000 psig for package type boilers, but 125 to 1000 psig is the most common range. See also section 4.5. Figure 3-2 shows a cutaway view of a typical small package type watertube boiler.

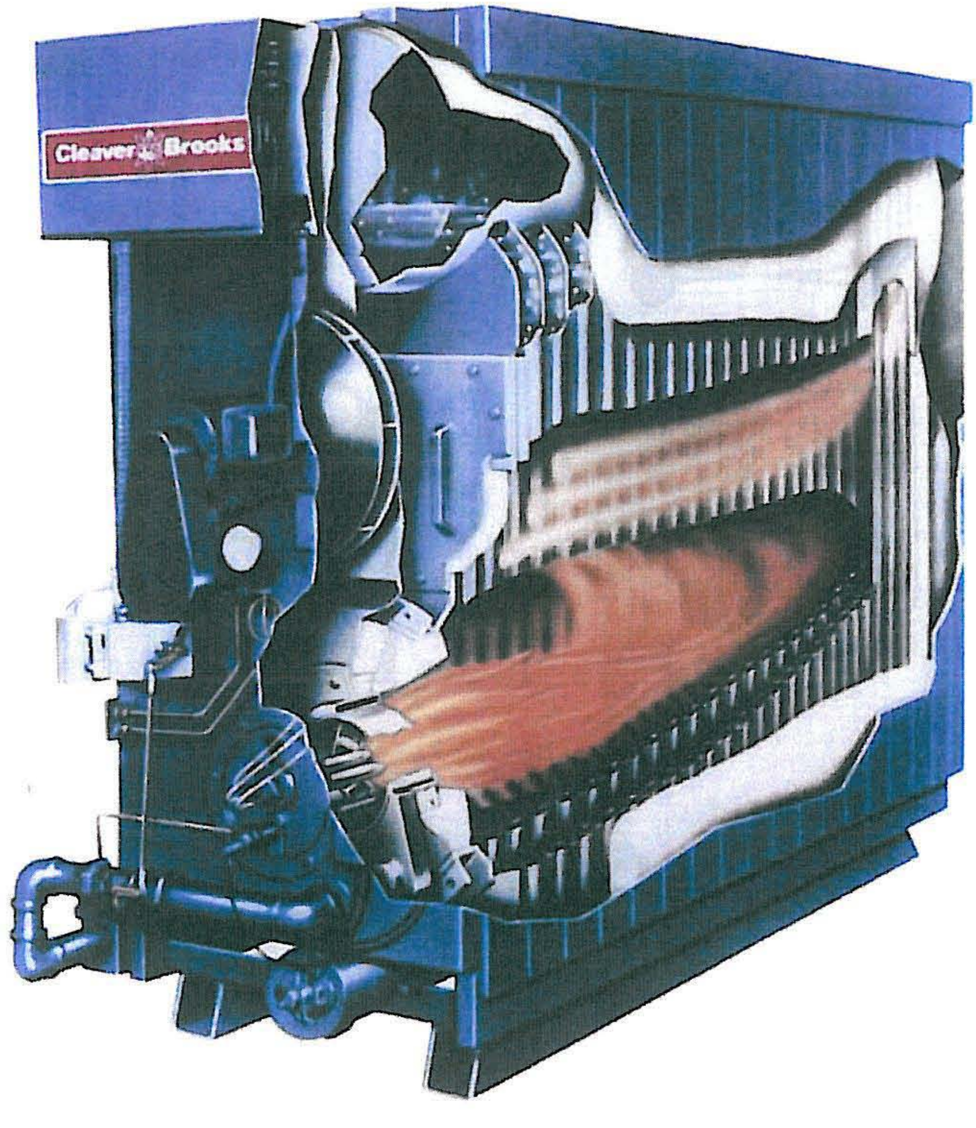
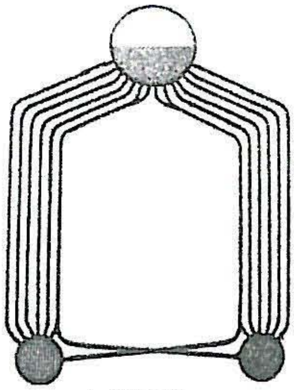


Figure 3-2. Cutaway view of a small package watertube boiler.

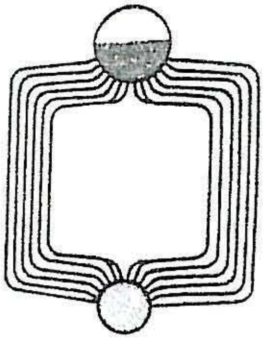
Watertube boilers can produce saturated, superheated or supercritical steam. These subjects are explained further in section 4.6 and 5.3.5 in this chapter.

3.2 WATER TUBE BOILER DESIGNS

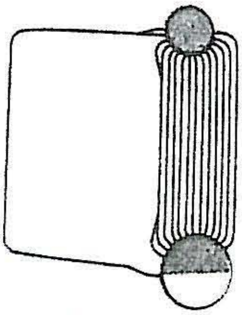
Watertube boilers come in three basic designs: A, D, and O type, as shown in Figure 3-3. The names are derived from the general shapes of the tube and drum arrangements. All have steam drums for the separation of the steam from the water, and one or more mud drums for the removal of sludges.



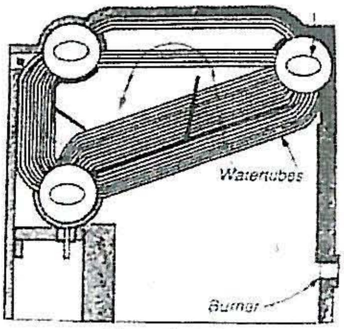
A – Type Boiler



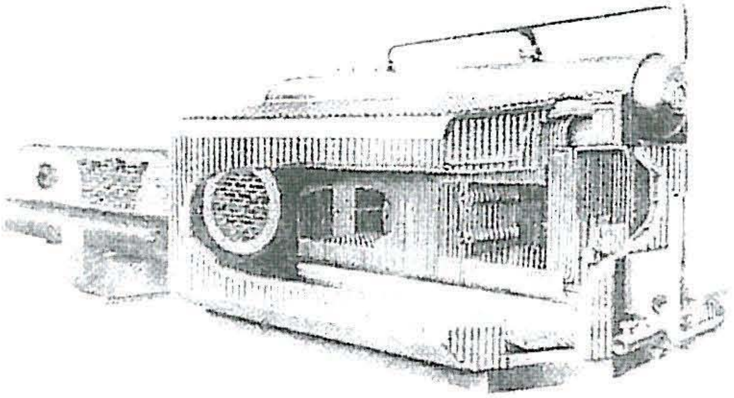
O – Type Boiler



D-Type Boiler



Water Tube Boiler



Industrial Package Boiler

Figure 3-3. Watertube boiler designs.

3.2.1 D Type Boilers

D type boilers have the most flexible design. These boilers have a single steam drum and a single mud drum, vertically aligned. The boiler tubes extend to one side of each drum. D type boilers generally have more tube surface exposed to the radiant heat than do other designs.

3.2.2 A Type Boilers

A type boilers have two mud drums symmetrically below the steam drum. This design is more susceptible to tube starvation if bottom blows are not performed properly because the two drums are each smaller than the single mud drums of D or O type boilers. Bottom blows should not be done at more than 80% of the rated steam load in these boilers. Bottom blow refers to the required regular blowdown from boiler mud drums to remove sludge and suspended solids.

3.2.3 O Type Boilers

O design boilers have a single steam drum and a single mud drum. The drums are directly aligned vertically with each other, and have a roughly symmetrical arrangement of riser tubes Circulation is more easily controlled, and the larger mud drum design renders the boiler much less prone to starvation due to flow blockage.

3.3 SPECIALTY STEAM BOILER APPLICATIONS

Some special applications of boilers require specific designs and operating procedures. These include waste to steam (trash to steam), waste heat recovery and heat recovery steam generators (HRSG).

3.3.1 Trash to Steam

Trash to steam boilers use trash (paper, plant material, plastics, etc.) as fuel. The steam is used for electrical power generation or central plant steam delivery. The main consideration is that the fuel has a widely varying heat value. Temperatures and heat fluxes can vary quite a bit over time. Water flows and the effects on chemical treatments can also vary widely. These units need more exhaustive monitoring and control

3.3.2 Waste Heat Recovery

If the waste heat stream is at 600°F or higher, then a boiler can be used cost-effectively to generate steam by recovering the heat value in the stream. Such boilers can be either watertube or firetube design.

3.3.3 HRSG Systems

Heat recovery steam generators (combined cycle), known as HRSGs, are typically used in combined cycle electric power generation. Waste heat from gas turbine exhaust is used to generate steam. The low temperature of the exhaust gases compared to direct fired units puts less stress on the boiler tubes. These units are typically constructed of lighter grade materials. The general design is a three drum configuration, as shown schematically in Figure 3-4. The low pressure (LP) drum is used as a deaerating feedwater heater. The intermediate pressure (IP) drum is used to generate steam for injection into the gas turbine. The high pressure (HP) drum is used to generate turbine steam for electrical power generation.

selected to match them. And certainly from

greater involvement in the steam cycle by major suppliers. As one example, companies that traditionally emphasized fired

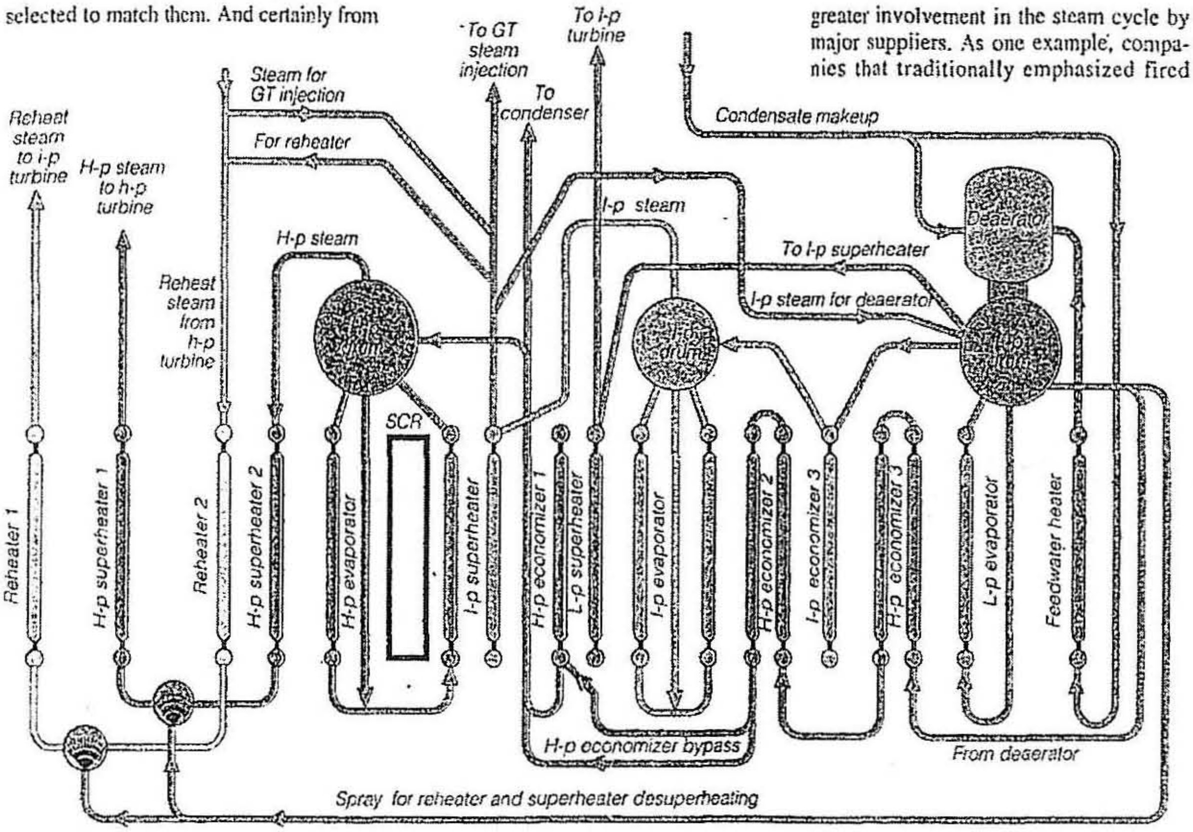


Figure 3-4. Schematic drawing of a typical HRSG design.

HRSGs require high purity water because of the use of the IP drum steam for turbine injection. Dissolved solids must be kept to a bare minimum in these units. The low skin temperatures lead to a relaxation in the allowable phosphate ranges for coordinated phosphate programs (section 7.4.1).

In a typical HRSG unit, the LP drum is treated with amines and oxygen scavengers, the HP drum is treated with a coordinated phosphate program, and the IP drum uses blowdown from the HP drum for some of the feedwater. This configuration requires careful balancing of the chemical treatment programs and control of boiler cycles. Chemical treatment is discussed in more detail in section 7.0.

3.4 SMALL WATER TUBE BOILERS AND STEAM GENERATORS

3.4.1 Systems

A variety of steaming boilers are found in commercial building and institutional heating systems, and in small industrial plants. These are usually package boilers with gas or oil firing, watertube or firetube design (Figures 3-1 through 3-6). Typical capacities range from a few hundred pounds of steam per hour to about 40,000 pounds per hour. Pressures range from 15 psig to about 300 psig. Some central utility plants for campus hospitals and high-rise housing developments, and many industrial plants, have boilers that operate in the 800 to 1000 psig range.

A variety of steam generating systems fall into this general category. As one example, some commercial buildings and campus power stations operate as cogeneration facilities. HRSG units (heat recovery steam generators) are used to make heating steam from the engine exhaust gases, using boiler feedwater from the common tank. Condensate from these systems is returned to the same tank.

Higher-pressure units often make turbine quality steam to drive generating turbines. Steam is taken off between turbine stages to heat secondary hot water or steam systems, and sometimes to drive HVAC chillers (chapter 4).

3.4.2 Operations

Small, low-pressure units will normally operate on city water makeup with no pretreatment. Newer units often have simple deaerating heaters, but most older systems depend entirely on chemical scavenging to remove dissolved oxygen. Makeup water and chemical treatment are fed to a common tank, which serves as a collection point for condensate, perhaps from several different systems.

Most higher-pressure units have deaerators and operate on softened or demineralized feedwater (chapter 2). These systems will have chemical feed points in the deaerator and the steam drum. Blowdown systems often include a small continuous blowdown and an intermittently operated manual blowdown. Feedwater quality varies widely with pressure range and end use application. Monitors and controls typically include a blowdown conductivity monitor.

Chemical treatment in these boilers includes, in addition to oxygen scavenging for corrosion control, calcium carbonate scale control in the boilers, and sometimes amine treatments for condensate corrosion control. Chemical treatment is discussed in section 7.0.

3.4.3 Cast Iron Boilers

These are small, low-pressure devices designed to generate heating steam and/or hot water for apartment buildings, small commercial installations, etc. Cast iron boilers consist simply of a firebox surrounded by a water chamber, such that heat is transferred directly from the firebox to the boiling water or to tube-type water heaters (sometimes called tankless water heaters). There are no boiler tubes per se. Figure 3-5 is a typical cutaway view of a cast iron boiler. Condensate return approaches 100 percent, so that there is little or no need for makeup water and the boiler water does not concentrate. Chemical treatment is similar to hot water systems (section 3.5 and chapter 4).

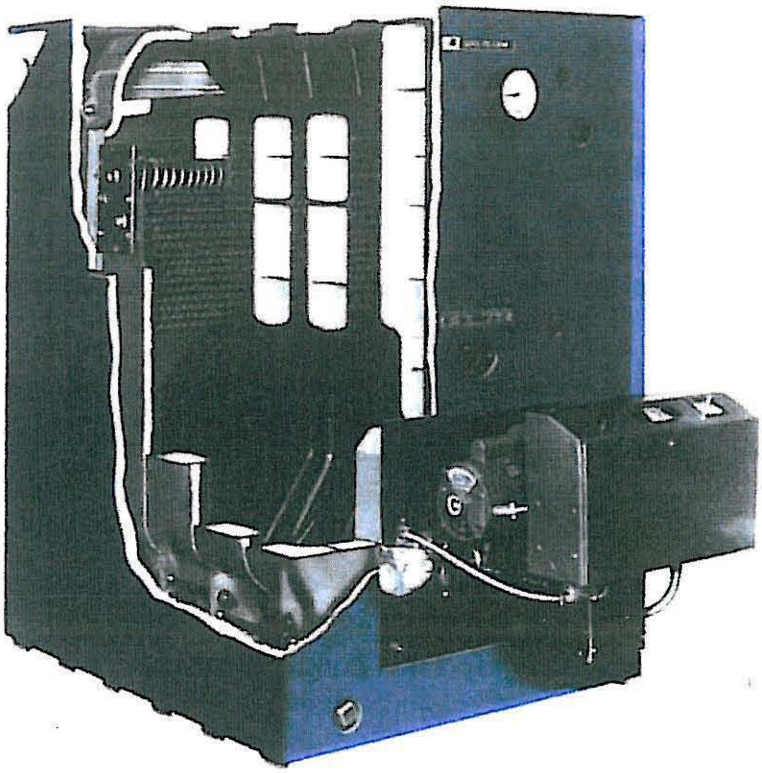


Figure 3-5. Cutaway view of a typical cast iron boiler.

3.5 FIRETUBE BOILERS

Original shell (tea kettle) boilers were improved upon by passing the hot gases through tubes inside the shell filled with water. This development marked the beginning of the firetube boiler as we know it today.

Firetube boilers are the mainstay of building steam heating systems, and are also used to drive small HVAC units. Their rugged design and limited pressure range means that they are forgiving, and thus relatively easy to operate. Firetube boilers are far less efficient than watertube boilers at generating steam because of the low ratio of heat transfer surface to water volume. Nevertheless, they find widespread use in simple heating applications or where service and maintenance capability is minimal.

The design is simple, as shown in Figure 3-6. They have no feedwater heaters, deaerators, or steam drums. The boiler shell is the steam drum. The large water storage capacity in the drum gives these boilers the ability to dampen the effects of sudden large changes in steam demand. However, because of this capacity, the time required for a firetube boiler to reach operating pressure from a cold start is considerably longer than for a watertube boiler.

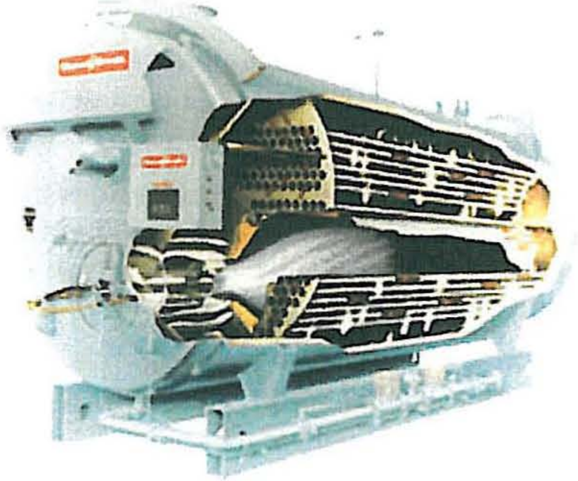


Figure 3-6. Cutaway view of a typical firetube boiler.

Firetube boilers normally produce 500-25,000 lbs of steam per hour at pressures from 5 to 250 psig. Shell strength is the limiting factor. The hot gas may make multiple passes through the shell (up to four passes). More passes increases fuel efficiency, but increases fan power consumption as well.

The ruggedness and low operating pressure range allows firetube boilers to use lower quality feedwater. At most, the makeup water will be softened, and many units use city water directly. Deaerators are often not used with firetube boilers, so that dissolved oxygen removal is accomplished with chemical oxygen scavengers alone.

Chemical treatment of firetube boilers is centered on corrosion control. In addition to oxygen scavengers, amines, and nitrites and/or molybdates are used for this purpose. Dispersants and chelants are seldom used. The programs are easy to maintain, consisting mainly of infrequent additions of chemicals. Chemical treatment is discussed in section 7.0.

3.6 HOT WATER HEATING BOILERS

3.6.1 Systems

Technically, hot water heating boilers are not boilers at all, since they run below the boiling point of water at operating pressure, and no steam is generated. They do, however, appear physically to be similar to firetube boilers. Pressures range from ambient (15 PSIG) up to about 50 PSIG.

Hot water heating boilers are more like home hot water heaters, except that the hot water is recirculated through the system. Components include a heater, a circulation pump, an expansion tank, and the heat exchangers or air handlers. Because there is no blowdown, there is no cycling in the system. From this point of view, hot water heating boilers are very similar to closed chilled water systems (chapter 4).

3.6.2 Circulation

Building hot water heaters are divided into several designs by circulation type, piping pattern, and temperature. Circulation is either natural or forced, and temperatures ranging from about 180 to 250 °F.

Natural circulation derives its motive power from the density differences of the supply and return water. Boiling water has a density of about 59.8 lb/cu.ft. and 70 ^{o}F water has a density of 62.3 lb/cu.ft. The hot water rises in the supply line and descends in the return pipe.

Forced circulation systems use booster pumps, satellite pumps, steam or air injection, or use superheated water, converted to steam in the heat exchanger, and then condensed in a cooler, or combinations of these.

3.6.3 Piping

Both one pipe and two pipe designs are used for circulating hot water for space heating. One pipe designs use a single pipe to circulate hot water from the heater to the air handlers, baseboard heaters, or radiators, and then back to the heater. There may be one or more series loops in a facility, with all the heating units in each loop in series. One pipe systems are the least expensive to install, but they cannot provide even heat distribution throughout the building, because the hot water cools as it passes through the system.

Two pipe designs have separate supply and return lines. Each heat exchanger is tied into each line with a tee, in parallel fashion. Two pipe designs are often combined in two or four pipe hot/chilled water systems. These designs use the same air handlers and fan coils for heating and cooling. Four pipe systems use separate pipes throughout, so that the chilled and hot water never mix, Two pipe systems use the same piping for hot and chilled water. In this case, the chemical treatments for the two systems must be identical or completely compatible.

3.6.4 Materials of Construction

Hot water piping systems are mostly carbon steel, with copper heat transfer tubes. Cast iron may be found in some older systems.

Many of these systems are, in fact, quite old. Problems resulting from age include localized corrosion resulting in leaks, and pipe diameter restrictions caused by calcite or iron oxide scaling, with resulting loss of heat transfer, lower flow rates, and increased corrosion.

3.6.5 Expansion Tanks

System pressure is maintained by an expansion tank, as in a chilled water system. In the steam cushion design, water from the boiler is flashed to steam in the expansion tank, and the pressure is controlled by the rate of expansion. These units are prone to water hammer as slugs of cold return water can lead to collapse of the steam cushion.

The gas cushion design uses inert gas to pressurize the expansion tank, thus maintaining steam pressure. In the mechanical cushion design, a pump and dump valve are used to maintain steam pressure in the tank as load changes. As the load decreases, the water heats up, increasing pressure in the expansion tank. The dump valve then opens to divert some water to an auxiliary tank. When load increases and pressure drops, the pump forces water back into the expansion tank.

4.0 Boiler Elements

This section deals with the subunits of the boiler cycle. Many of the elements are covered in section 2 (pretreatment). The various elements are discussed in this section primarily to relate them to the boiler operation itself. Strictly speaking, the boiler is only the section in which heat is applied to the water to convert it to steam, and the associated drums and controls that regulate water flow, steam flow, fuel flow, air flow, monitoring and chemical injection. However, this section will also deal with the other important elements of the steam cycle so that the operation of the boiler is understood in terms of mass and energy balance, which must include inlets and outlets.

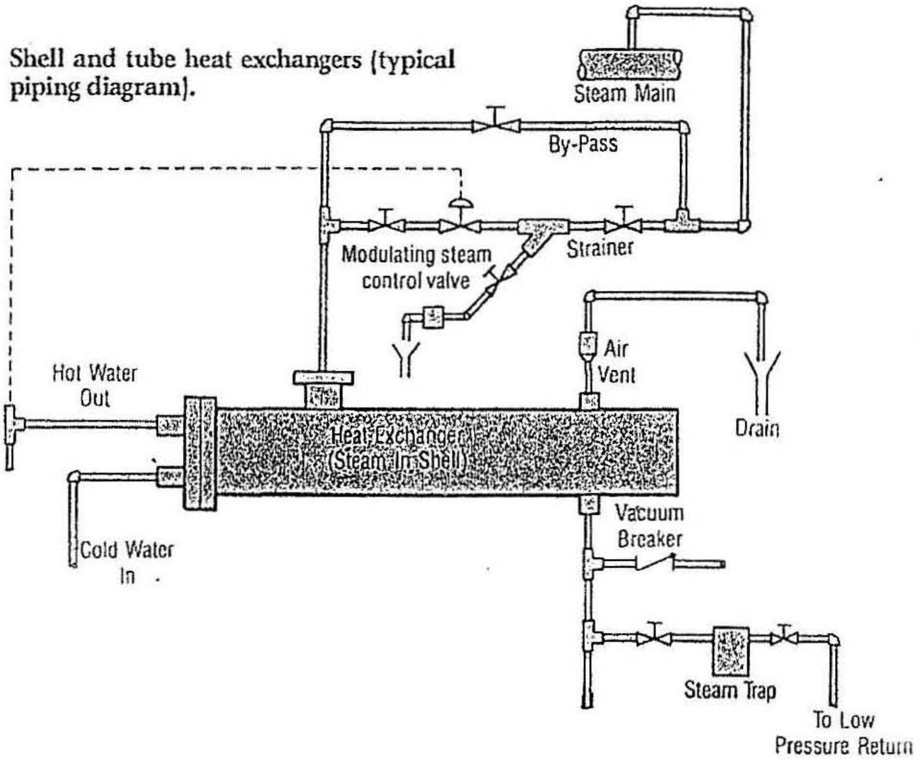
4.1 THE BOILER CYCLE

Section 2.2 explains the steam cycle from the water point of view. In general, water is recycled in a boiler circuit. Since the water completes a cycle, it is possible to start at any point and traverse the circuit. It is usually most useful to start with the condensate or makeup water, and proceed in the direction of flow. The main elements are the condensate pump, preheaters, deaerator, boiler feed pump, economizer, boiler, superheater, attemperator, load, condenser and back to the condensate pump. Many different combinations of these components are found operating boiler systems.

In addition there is a set of controls to monitor water and steam flow, fuel flow, air flow, and chemical treatment additions. Sample points may exist at a number of places, most typically the condensate, deaerator outlet, feedwater (often the economizer inlet), boiler, saturated steam, and superheated steam. Each sample point flows to a conditioner, which comprises one or more coolers, valves, filters (optional), and flow controllers.

4.2 FEEDWATER HEATERS

Boiler efficiency is improved by the extraction of waste heat from spent steam to preheat the boiler feedwater. Heaters are shell and tube heat exchangers with the feedwater on the tube side (inside) and steam on the shell side (outside), as shown in Figure 3-7. The heater closest to the boiler receives the hottest steam. The condensed steam is recovered in the heater drains and pumped forward to the heater immediately upstream, where its heat value is combined with that of the steam for that heater. Ultimately the condensate is returned to the condensate storage tank or condenser hotwell.



Shell and tube heat exchangers (typical piping diagram).

Figure 3-7. A simple feedwater heater circuit.

A typical arrangement for feedwater loops is to have three low-pressure feedwater heaters. They will heat the condensate to just below the atmospheric boiling point of water. The fourth heater is usually a deaerator where live steam is directly injected into the feedwater for oxygen removal. It will typically be at an exit temperature just above the boiling point of water at atmospheric temperature. Then there will be another two or three high-pressure feedwater heaters. The final heater will have an exit temperature within 50 to 100 degrees of the boiler temperature.

4.3 DEAERATORS

Feedwater will often have oxygen dissolved in it at objectionable levels. The oxygen comes from air in-leakage from the condenser, pump seals, or from the condensate itself. The oxygen is mechanically removed in a deaerator, sometimes referred to as a deaerating heater in smaller systems.

Deaerators work on the principle that oxygen is decreasingly soluble as the temperature is raised (Figure 3-8 and chapter 1). Separation of the dissolved oxygen from the water is accomplished by creating a head space and by passing a stripping stream of gas (steam) through the feedwater. There are two basic designs for deaerators, spray and tray type.

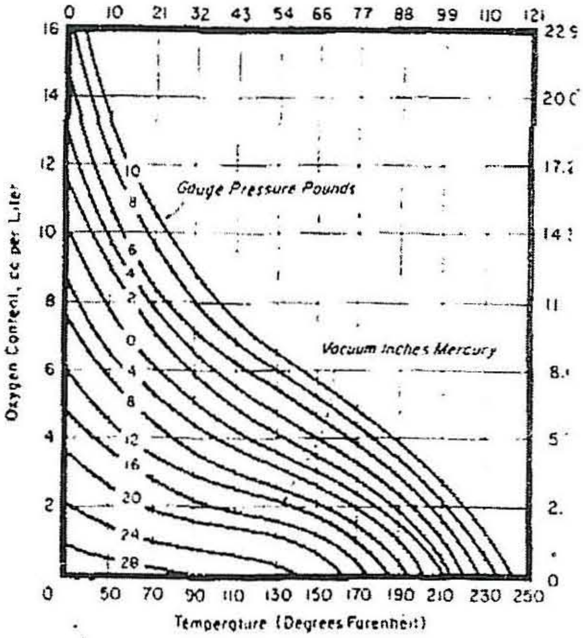


Figure 3-8. Oxygen solubility vs. temperature

4.3.1 Tray Deaerators

Water is introduced into a vertical tank. Trays are arranged in a vertical stack in this tank. The water overflows from one tray to the next below it until it enters the storage section. Oxygen removal is accomplished by contacting the water with steam at about 15 psig. The steam flow is either counter current with the falling water or co-current

In countercurrent designs, the entering steam contacts the hottest and most oxygen free water, and passes successively to the cooler more oxygenated water. As a consequence oxygen removal is more efficient, but heat transfer suffers. Water holdup in the trays can be a problem in counter flow designs. Figurer 3-9 shows a common counterflow deaerator.

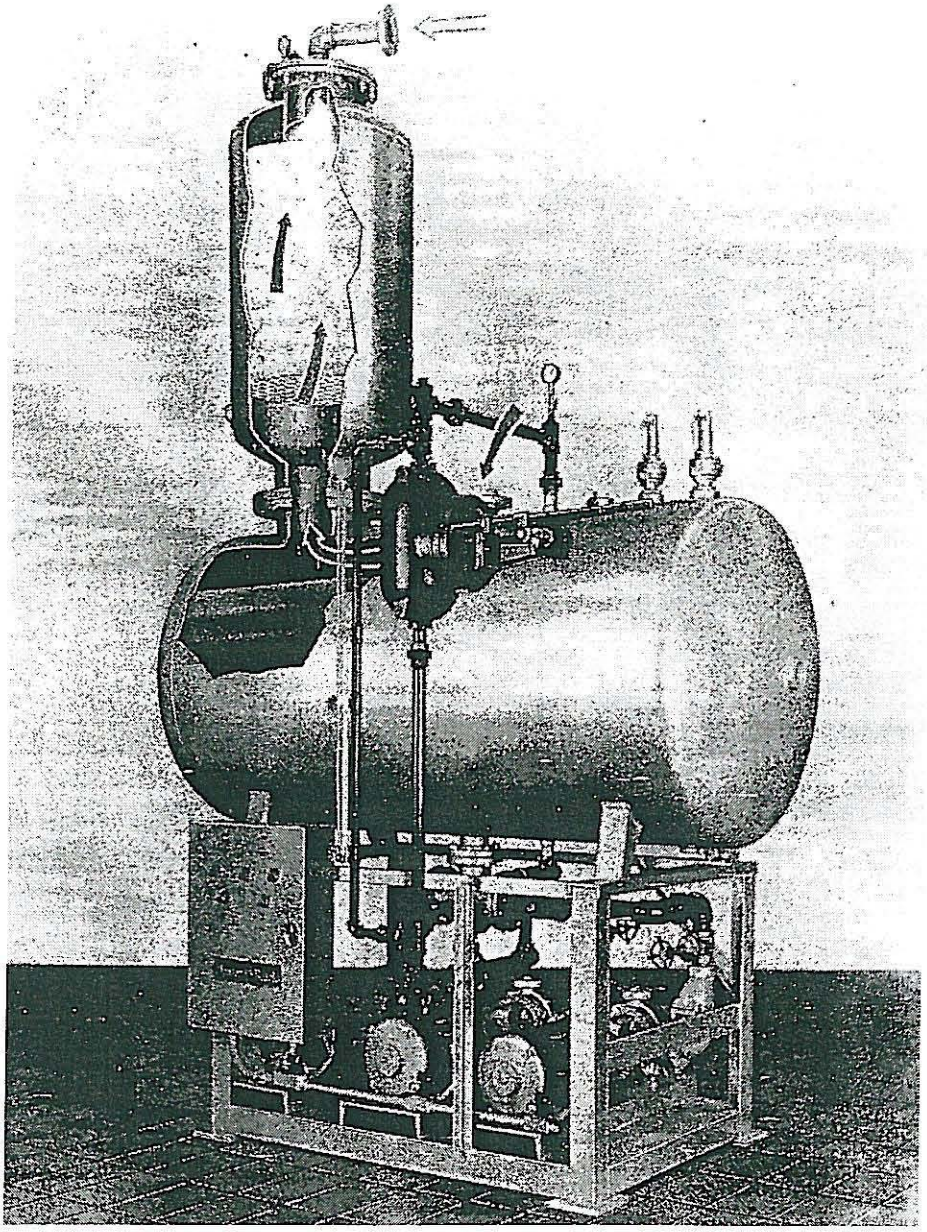


Figure 3-9. A small counterflow deaerator.

In co-current designs, the steam and water flow in the same direction. Heating is more efficient because the coldest water contacts the hottest steam, but the most oxygen laden steam contacts the most oxygen free water, and so tends to produce a less effectively deoxygenated water.

The trays can have drip holes which allow the water to break into small droplets as it cascades down the deaerating section. Plugged drip holes reduce operating efficiency. Rising steam flows through bubble caps to develop a more intimate mixing of the steam with the water, increasing gas stripping efficiency.

Tray deaerators are susceptible to mechanical failure where the trays are welded into the supports. Also, they can be a source of corrosion products in the feedwater. To avoid this, the tray section is often made of stainless steel.

4.3.2 Spray Deaerators

Spray designs rely on the direct contact of the steam with fine droplets of feedwater produced by a "shower head" spray system inside the deaerating tank. Again, the design can be counter or co-current flow, with the same effects.

Spray deaerators are more efficient at oxygen removal than tray designs. In both designs, oxygen removal takes place at the water/steam interface. In tray deaerators, the available surface area is not great, so that the rate of oxygen removal is low. In spray designs, the available water surface area is much larger, thus increasing the oxygen transfer rate from the water to the steam.

4.3.3 Deaerator Storage Tanks

The deaerated feedwater enters a storage tank. The tank serves several purposes. Since the pump head is broken at the deaerator because of the head space, the deaerated water must be pumped to the boiler. The tank serves as a level control device to prevent starvation of the boiler feed water pump. A float type level controller adjusts the amount of feedwater entering the deaerating section.

Often, oxygen scavenging chemicals are added to further reduce the oxygen residuals in the feedwater. The tank provides a residence time for contact of the chemicals with the water. This improves the effectiveness of the oxygen scavengers. Usually a ten-minute supply of water is in the deaerator storage tank, but residence time should be adjusted based on steam demand and variability.

4.3.4 Deaerator Performance

Deaerators are supposed to be able to achieve 7 parts per billion of oxygen, or 0.005 cc of oxygen gas at standard temperature and pressure (STP) per liter of water: This calculation involves converting ppb solids to cc. of gas:

$$7 \text{ ppb} = 7\text{x}10^{-6} \text{ g/l}$$

$$7\text{x}10^{-6} \text{ g/l x 1 mole/32 g x 22.4 l/mole}_{@STP} \text{ x 1000 cc/l} = 0.005 \text{ cc/l}$$

Actual performance is in the range of 5 to 25 ppb for spray and 20 to 40 ppb for tray deaerators. The water should be heated to within 2-4 °F of the saturation temperature. The steam exits through a vent, which typically controls the unit at a positive pressure of about 0.5 psig. This means that the water leaving the deaerator is at a temperature of 214 to 216 °F at one standard atmosphere of ambient pressure.

Efficient performance requires the temperature to be slightly above the boiling point of water at ambient pressure, but not too much above that point or else heat value is wasted.

Deaerators will remove other noncondensible gases such as nitrogen, and also carbon dioxide, but carbon dioxide removal is much less efficient. Carbon dioxide reacts with water to form nonvolatile bicarbonate ions. In the normal 8.0 to 8.5

operating pH range for deaerators, most of the carbon dioxide in the water is present as bicarbonate. Although the equilibrium reactions should allow the bicarbonate to decompose and strip, this reaction rarely goes to completion. See chapter 1 for a discussion of the carbon dioxide equilibrium system in water.

The non-condensable gases and steam are vented from the deaerator through a tube with either a valve or a machined orifice plate to regulate the flow. A valve is preferable in units with a wide range of steaming rates. The steam vent should be sized to permit efficient flow of exiting non-condensable gases and a slight excess of steam, so as to maintain a small positive pressure in the deaerator. Poor deaerator performance is often traceable to a vent that is too big for the feedwater flow. A good test is to be able to see an invisible area at the vent exit before a plume of steam plus water droplets appears. Poor mechanical deaeration will lead to higher chemical costs for oxygen scavengers, and generally result in excessive metals transport into the boiler.

The use of chemical oxygen scavengers can produce feed water containing 5 ppb or less of dissolved oxygen. Oxygen scavengers are discussed in section 7.2.

The steam required for deaeration is about 1% of the feedwater flow for every ten degrees of temperature rise in the deaerator:

$$\text{Steam required (lb/hour)} = (T_{out} - T_{in}) \times 0.01 / 10^{\circ}\,\text{F} \qquad (3\text{-}1)$$

This is only an approximation, as the enthalpy (heat content) of the steam and water will vary somewhat with actual operating temperature.

4.4 ECONOMIZERS

Economizers are the last stage of the feedwater system. They are designed to extract heat value from exhaust gases to heat the steam still further and improve the efficiency of the boiler. They are simple finned tube heat exchangers. Economizers are prone to corrosion due to their high surface area. Often residual oxygen in the feedwater is removed by a corrosion process in the economizer. Economizers are also susceptible to failure from the hot side due to impurities in the hot gas stream. Figure 3-10 shows an economizer and superheater design in a large industrial boiler.

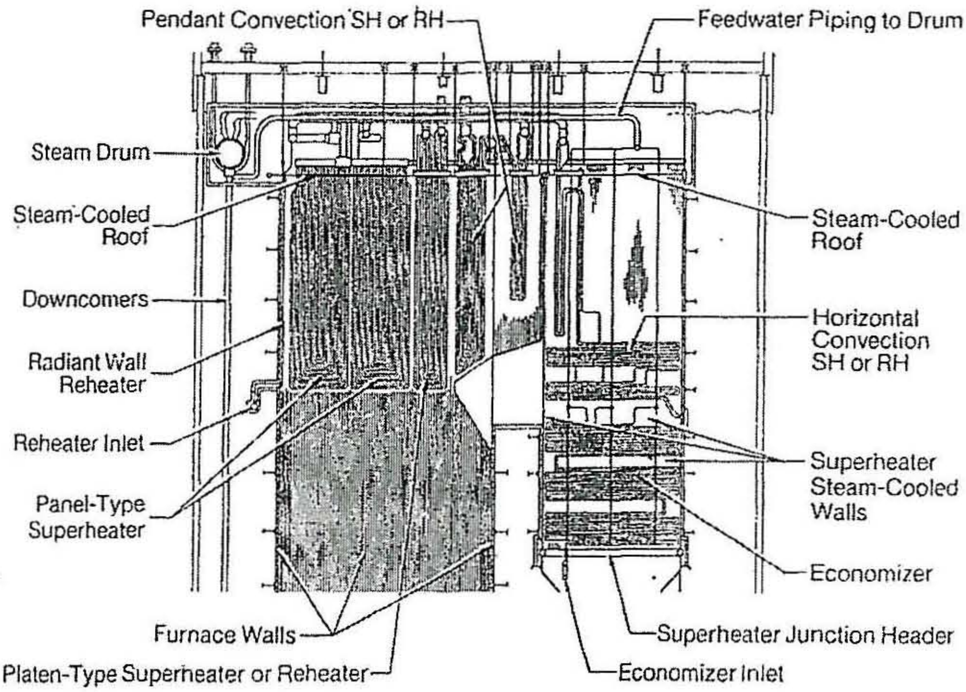


Figure 3-10. Economizer and superheater design in a large industrial boiler.

Not all boilers have economizers. Usually they are found only on water tube boilers using fossil fuel, as an energy conservation measure.

4.5 WATER TUBE BOILERS

The boiler is the section in which heat transfer from the fuel to the water takes place. Firetube boilers do not have a separate boiler drum, as the shell itself is the steam separation chamber and recirculation is not an issue.

In a watertube boiler there are several design factors. These involve the type of fuel and the method of firing, the arrangement of the boiler tubes, the manner of water circulation, and the arrangement for the separation of the steam from the water.

4.5.1 Design Principles for Water Tube Boilers

Feedwater enters the boiler steam drum from the economizer, or from the feedwater heater train if there is no economizer. The cooler feedwater helps create the circulation in the boiler. Cooler water in the downcomers, which are outside the heat transfer area, sinks and enters the mud drum through a bottom header. The water is heated in the heat transfer tubes and forms steam. The steam - water mixture is less dense than water and so rises in the riser tubes to the steam drum. Boiler circulation is discussed in section 4.5.2.

The steam drum is a horizontal cylinder containing internal elements for feedwater entry, chemical injection, blowdown removal, level control, and steam- water separation. The boiler water typically is at a level of about one half the diameter of the cylinder. The steam bubbles disengage from the boiler water in the riser tubes and steam flows out from the top of the drum through steam separators.

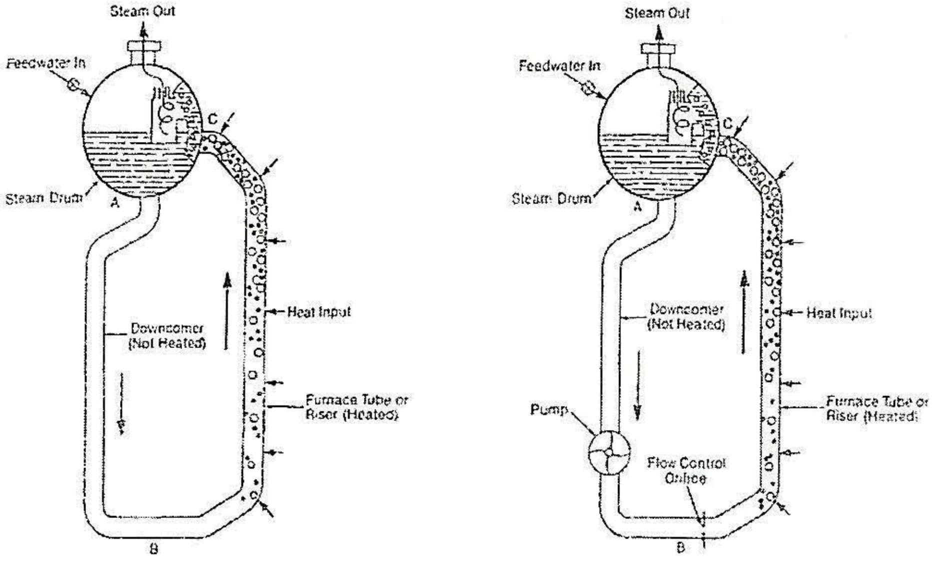
The function of the steam separators is to minimize physical carryover of water droplets from the steam in the drum. This is needed because the boiler water contains many non-volatile substances that will create problems if carried over into the steam.

The lower, or mud drum is connected to the steam drum by a set of riser and downcomer tubes. The mud drum acts to concentrate solids such as salts formed from hardness and silica or corrosion products carried into the boiler. Colder, dense water flows to the mud drum through a small number of downcomer tubes, and rises to the steam drum through a much larger number of riser tubes.

Blowdown is taken from the upper drum, where the water is more concentrated and removal of dissolved solids is more efficient. Bottom blows from the mud drum are usually carried out intermittently for brief periods, to effect removal of the accumulated suspended solids. Blowdown can be continuous or intermittent in the steam drum depending on the water quality, steam load, and makeup water capacity of the external treatment train.

4.5.2 Forced vs Natural Circulation

The difference in these designs is based on the overall space requirements and boiler tube design (Figure 3-11). Natural circulation units produce a head difference between the downcomer tubes and riser tubes sufficient to overcome frictional resistance to flow in the risers, and produce a velocity of circulation sufficient to maintain the necessary steam flows. The flow of water should be about ten times the steam flow rate, or a recirculation ratio of ten to one.



(a) Simple Natural or Thermal Circulation Loop

(b) Simple Forced or Pumped Circulation Loop

Figure 3-11. Natural and forced boiler water circulation.

The density difference between the cold downcomer water and the steam laden riser tube water provides the driving force. The force producing flow is the product of density difference in the cold downcomer water and the steam-water mixture in the riser tubes times the height of the tubes. If this force is sufficient to overcome flow resistance in the riser tubes the water will circulate naturally.

Sometimes, however, the force is not sufficient to produce a rapid enough flow in the riser tubes to prevent excessive steam buildup in the risers. A circulation pump is used to boost the flow to the needed levels. This is a forced circulation design. Forced circulation is often employed at higher operating pressures where the steam - water mixture density in the risers is not too much different from the downcomer density. A low recirculation ratio will increase the proportion of steam at the top of the riser tubes. If the steam is more than about 20% by weight in the riser tubes, steam blanketing of the tubes can become a problem. Blanketing occurs when so much steam is generated in the riser tubes that it prevents water from reaching the tube walls. This leads to overheating of the riser tubes, to chemical concentration effects causing deposit formation and/or corrosion.

4.5.3 Steam Drums

The steam drum performs several functions:

2. Mix the feedwater with the saturated water.
3. Mix water treatment chemicals
4. Purify the steam
5. Remove blowdown water
6. Accommodate rapid changes in steam flow rates
7. Serves as a collection point for the steam generated in the riser tubes.

The main purpose of the steam drum is to permit efficient steam disengagement from the boiler water. The large surface area at the water level in the drum allows for rapid separation of the steam bubbles entering the drum from the riser tubes.

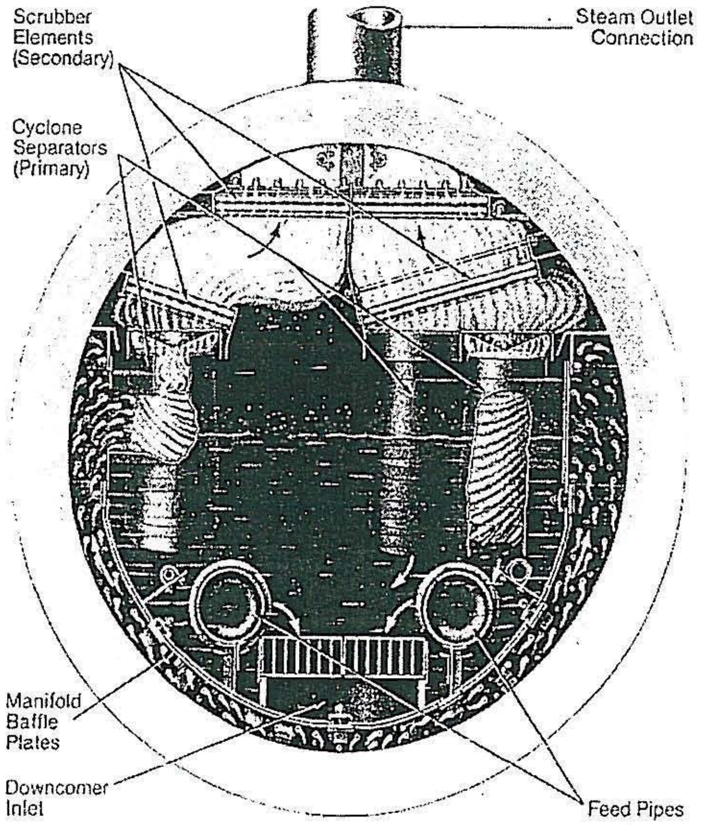
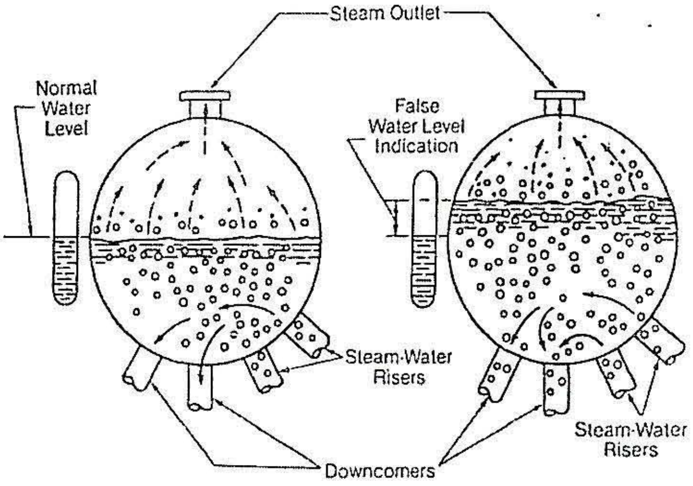


Figure 12. Steam drum internals.

Internal features of a typical steam drum are shown in Figure 3-12. Boiler water enters the steam drum from the riser tubes, and a baffle plate minimizes agitation from the surge. Feedwater enters the drum via a pipe running the length of the drum and near the bottom. Chemical feed enters through a tube near the water surface. Steam flows to separators, where excess entrained water droplets are separated from the steam by path changes and the momentum differences between the water droplets and the gas stream.

Level control in the steam drum is a complex matter. When steam load is increased one would expect the drum level to initially drop because of the greater mass leaving the drum than entering it. However, the pressure drop causes the entrained steam bubbles to swell, and the drum level initially rises. The opposite effect is seen when steam load is decreased. These effects are illustrated in Figure 3-13.



(a) Low Steaming Rate (b) High Steaming Rate

Figure 3-13. Effect of load on steam drum water level.

A single element level controller can cause serious problems, especially in the case of steam load increases. The initial swelling causes the feedwater flow to drop, leading to even more swelling until the drum may actually dry out. A two element controller, that uses level sensing and steam flow sensing can provide for more reliable level control.

4.5.4 Mud Drums

By contrast the mud drum is quite simple. It is a cylinder or cylinders, often smaller in diameter than the steam drum, and connected to the steam drum via downcomer and riser tubes (Section 3.4). Suspended solids, such as precipitated hardness, silica, and corrosion products preferentially accumulate in this section, and are removed by bottom blowdown. A typical bottom blow operation is a once per shift opening of the blowdown valve for a few seconds.

If solids are allowed to accumulate in the mud drum, the riser tubes can be blocked. The resulting flow restrictions can lead to tube failures from overheating. There is no practical way to determine the level of solids buildup in the mud drum or bottom header without a visual inspection, so proper periodic blowdown is very important.

4.5.5 Boiler Tubes

Boiler tubes are usually fabricated from high strength carbon steel. The tubes are welded to form a continuous sheet or wall of tubes. Often more than one bank of tubes is used, with that bank closest to the heat source providing the greatest share of heat transfer. They will also tend to be the most susceptible to failure due to flow problems or corrosion/deposition problems

Some boiler tubes are rifled to provide better heat transfer efficiency. The rifling creates more turbulence, and so minimizes deposition and corrosion problems.

Deposits build up on the boiler tubes by corrosion processes and precipitation of sparingly soluble salts. Both of those processes occur preferentially on the hot side of the tubes (the side facing the heat source). As steam bubbles form, the surrounding water is more concentrated with salts and suspended solids. If the solubility is exceeded the material will come out of solution and deposit on the walls.

A good measure of water treatment performance is the determination of deposit weight density. During maintenance inspections, tubes are cut from various parts of the boiler. The tubes are split along the hot-cold side boundary. A portion of the tube is cleaned by chemical or mechanical means, and the amount of removed material is determined by mass balance. The deposit weight density is the weight of removed deposits divided by the surface area from which they were obtained. In addition, chemical analysis is used to determine the makeup of the deposits.

Deposit Weight Densities should be reported by hot vs cold side measures, and a historical record should be maintained so as to be able to determine the rate of buildup, the nature of the deposits, and to identify any unique events. Chemical cleaning is recommended when deposit weight densities approach certain values (Table 3-1). Chemical cleaning should be performed by an experienced provider as damage to the boiler or environmental and safety problems may result.

Table 3-1
Recommended Deposit Weight Densities For Cleaning

Operating Pressure (psig)	Deposit Weight Density (g/ft^2)
<1000	20 to 40
1000 to 2000	12 to 20
> 2000	10 to 12

The values in Table 3-1 are based on mechanical scraping methods. Other methods may result in a greater of lesser bias, and should be adjusted accordingly. There are on-line thermocouple methods for evaluation of deposit buildup. These methods are expensive to install, and may create integrity problems for the tubes so equipped.

4.6 SUPERHEATERS

The superheater is not a part of the boiler. It is a heat exchanger placed after the steam exit of the boiler. The purpose of the superheater is to remove all moisture content from the steam by raising the temperature of the steam above its saturation point (see Figure 3-10).

Steam leaving the boiler is saturated: that is, it is in equilibrium with liquid water at boiler pressure (temperature). Any work done by the steam entails a loss of energy of the steam, and a portion of the steam must condense back to liquid water. For every thousand BTUs of heat lost (= 0.293 kilowatt-hours) one pound of water will condense from the steam. Energy losses come about by work, frictional losses in the steam line, radiation losses through the walls of the vessels, and conductive losses by contact with the process.

The superheater adds energy to the exit steam of the boiler. It is a single bank of tubes either in a horizontal or vertical arrangement that is suspended in the convective or radiation zone of the boiler. The added energy raises the temperature and heat content of the steam above the saturation point. In that case, energy losses by the steam will not result in condensation until the saturation temperature of the steam is reached. The main consequences of superheated steam are that the lack of moisture precludes corrosion in the steam lines. In the case of turbines, excessive moisture in the steam can adversely affect the efficiency and integrity of the turbine. Superheated steam has a larger specific volume as the amount of superheat increases. This necessitates larger diameter pipelines to carry the same amount of steam.

Superheaters are not intended to experience moisture. As such they do not have drains, or other means to clean them. It is important that the steam be of high purity and low moisture content (entrained water droplets) so that non-volatile substances will not build up in the superheater. Although it is not recommended, superheaters can be cleaned in place, but it is necessary to thoroughly rinse the tubes with high purity water.

4.7 ATTEMPERATORS

Attemperation is the primary means for controlling the degree of superheat in a superheated boiler. Attemperation is the process of partially desuperheating steam by the controlled injection of water into the superheated steam flow.

Superheaters are not controllable. The degree of superheat will depend on the steam load and the heat available, given the design of the superheater. The degree of superheat of the final exiting steam is generally not subject to wide variation because of the design of the downstream processes. In order to achieve the proper control of superheat temperature an attemperator is used.

A direct contact attemperator injects a stream of high purity water into the superheated steam, as shown in Figure 3-14. The attemperator is usually located at the exit of the superheater, but may be placed in an intermediate position. Usually, boiler feedwater is used for attemperation. The water must be free of non-volatile solids to prevent objectionable buildup of solids in the main steam tubes and on turbine blades.

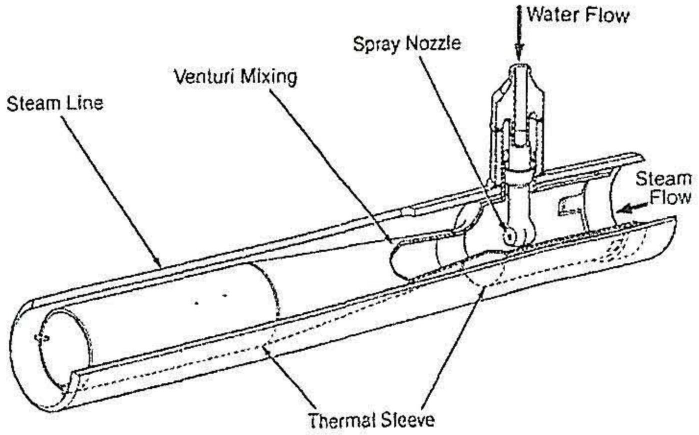


Figure 3-14. A steam attemperator design.

Water entering the superheater steam vaporizes, and the absorption of heat to vaporize the water lowers the superheat temperature to the desired point. A feedback controller operates the attemperator inlet valve to control the temperature. The water enters the superheater via a conical thermal sleeve insert oriented downflow. This prevents the contact of water droplets with the superheater tube, preventing erosion corrosion. Entry is usually at an intermediate point in the superheater, between sections, or at the outlet.

Since attemperator water comes from the boiler feedwater, provision for it has to be made in calculating flows. The calculation is based on heat balance. The total enthalpy (heat content) of the final superheat steam must be the mass-weighted sum of the enthalpies of the initial superheat steam and the attemperation water:

M_w = mass of the attemperation water
M_s^o = mass of the superheated steam before attemperation
M_s^f = mass of the final steam flow = $M_w + M_s^o$
h_w = enthalpy of the attemperation water (at the temperature at the takeoff) = BTU/ lb
h_s^o = enthalpy of the initial superheated steam
h_s^f = enthalpy of the final superheated steam

Then, using these definitions:

$$M_w = M_s^o (h_s^o - h_s^f) / (h_s^f - h_w) \qquad (3\text{-}2)$$

Example: assume a steam flow of 100,000 pounds per hour of saturated steam from the boiler at 480 psia. The initial superheat temperature is 800°F (337 degrees of superheat), and the final superheat temperature is to be controlled at 650°F (187 degrees of superheat). The attemperator takeoff is at 400°F.

From steam tables, $h_w = 424.17$, $h_s^o = 1413.6$, and $h_s^f = 1330.5$ (BTU/lb)

Then using equation 3.2.7.1:

$$M_w = 100{,}000\ (1413.6 - 1330.5) / (1330.5 - 424.17)$$

$$M_w \cong 9170 \text{ pph}$$

Then, the total feedwater flow needs to be 100,000 + 9170 ≅109,200 pph

4.8 CONDENSATE SYSTEMS

Although not a part of the boiler per se, condensate will usually find its way back to the boiler as part of the feedwater. Accordingly, one must take into account the amount and quality of the condensate when calculating boiler treatment parameters. In this section topics to be considered are collection and storage systems, the use of returned condensate, and condensate polishing.

4.8.1 Steam/Condensate System Design

In a complex steam distribution system there will be several components. These will include heat exchangers, process equipment, flash tanks, and storage tanks.

Heat exchangers are the places in the system where steam is used to heat a process or air by indirect contact. Shell and tube exchangers are the usual design, with steam usually on the shell side. The steam enters as superheated or saturated and may leave as superheated, saturated, or as liquid water, all depending on the initial steam conditions and the design load of the exchanger.

Process equipment usually means turbines, whether used for power generation, HVAC equipment, air compressors, or turbine pumps. Jacketed reactors heated with steam are also, obviously, process equipment.

Flash tanks are components whose function is to recover heat value from condensate or blowdown, and to produce a cleaner condensate. Water enters the flash tank at elevated temperature, and the pressure is reduced to below the saturation pressure at the temperature of the water. A portion of the water is converted to steam, and the steam can then be used for further processes. That steam will be condensed, and depending on the process, may be usable as feedwater. For example, blowdown can be flashed to recover a portion of the water as clean condensate at elevated temperature. This will improve the economics of making fresh makeup water and heating it to feedwater temperatures.

The calculation of flows is based on heat balance. The enthalpy of the exiting steam and water will sum up to the enthalpy of the initial water on a mass-weighted basis.

M_w = mass of high temperature water entering the flash tank
M_s = mass of steam leaving the flash tank
h_w^o = enthalpy of the entering water
h_s = enthalpy of the exiting saturated steam at the flash tank pressure
h_w^f = enthalpy of the exiting water.

Then, using these definitions:

$$M_s = M_w (h_w^o - h_w^f) / (h_s - h_w^f) \qquad (3\text{-}3)$$

flow of blowdown of 1000 pph at a temperature of 450°F (435 psig saturated steam) to a flash tank. The pressure is reduced to 90 psig (75 psia, 308°F). Then from steam tables

$$M_w = 1000,\ h_s = 1182,\ h_w^{o} = 430,\ h_w^{f} = 278 \text{ (BTU/lb)}$$

$$M_w = 1000\,(430 - 278) / (1182 - 278) \quad \text{(equation 3.2.8.1.1)}$$

$$M_w = 168 \text{ pph}$$

So that 168 pph of 90 psig steam is made available, and 832 pounds of blowdown at 308° F is available for makeup water preheating.

Note the similarity of this calculation to the attemperation water calculation in equation (3-2).

4.8.2 Condensate Reuse

Condensate is often re-used as part of the feedwater for boilers.

When condensate is suitable for re-use, it saves the cost of producing and heating feed water. Condensate may also contain some boiler treatments such as neutralizing amines and oxygen scavengers, saving the cost of replacing these chemicals, and it is usually lower in dissolved oxygen content than makeup water. In calculating the chemical feed requirements for feedwater, the amount of condensate returned is important.

Percent condensate returned is expressed as the percentage of the main steam produced by the boiler returned as condensate:

M_s = steam rate (pph)
M_{BD} = blowdown rate
M_f = Feedwater rate
$\%BD = M_{BD} / M_f$ (expressed as a decimal fraction)
C = boiler cycles = $M_f / M_{BD} = 1/ \% BD$
CR = condensate returned as feedwater
$\% CR = 100\,(CR / M_s) = 100\,(CR / M_{BD}\,(C-1))$
M_{MU} = makeup water (external treatment)
$M_f = M_{MU} + CR$ (mass balance on makeup, feedwater and condensate return)

Problem: How much hardness will there be in the feedwater if the makeup water contains 25 mg/L hardness as $CaCO_3$, the steam rate is 40,000 pph, the boiler cycles are 10, and the percent condensate returned is 50%?

Calculate the feedwater:

$$M_f = M_s + M_{BD} = M_s + M_f/C = M_sC / (C-1)$$

$$M_f = 44{,}444 \text{ pph}$$

Calculate the condensate:

$$CR = 0.5M_s = 20{,}000 \text{ pph}$$

Calculate the Makeup Water:

$$M_{MU} = M_f - CR = 44{,}444 - 20{,}000 = 24{,}444 \text{ pph}$$

The makeup is 55 % of the feedwater, so the hardness will be 25 mg/L x .55 =14 mg/L

Chemical treatment to the boiler should be based on 14 mg/L hardness

4.8.3 Condensate Polishing

This topic is discussed in more detail in Chapter 2. Condensate is not always suitable for re-use as is. The condensate is routed through pipes that may be corroding, or it may be contaminated by contact with process leaks. Often high levels of iron, copper, hardness, and organic chemicals may be contained in the condensate.

The ability to re-use the condensate will depend on what measures are taken to purify the condensate relative to the boiler feedwater limits (see section 7.2).

Condensate is polished by ion exchange and filtration processes. The condensate must be cooled below about 140° F for use with an ion exchange resin. The equipment is either a deep bed mixed bed polisher, or a powder resin polisher (see chapter 2). Figure 3-15 shows a typical condensate polishing system.

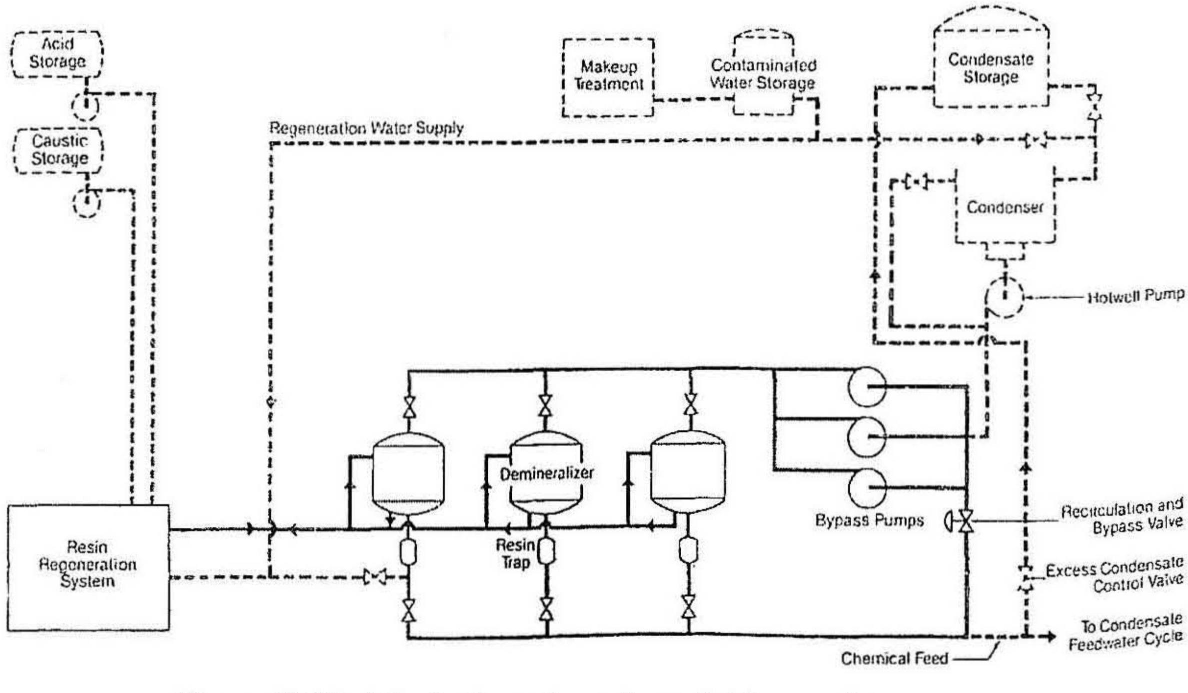


Figure 3-15. A typical condensate polishing system.

In the deep bed unit, a blend of strong acid cation resin and strong base anion resin is used. The bed depth is typically twice that of a demineralizer unit, and utilizes flow rates per unit area of about 3 to 10 times that of a demineralizer. Regeneration is ex-situ, the resin is separated and sluiced to a separate unit for regeneration. Then the resin is returned to the polisher vessel, air mixed, and returned to service or placed in standby.

The powder unit is a vessel with a series of wire wound collector pipes. A slurry of a blend of powdered anion and cation resin is mixed in the tank, and then quickly filtered to form a thin ion exchange powder coating on the collector elements. The collectors act as particulate filters and ion exchange polishers. The polishing capacity is small, however.

Most polishers function more as particulate filters, and usually exhaust on pressure drop rather than ion exchange capacity. The powder units are used where particulate filtration is the most critical function. They are cheaper to use, as they are not regenerated, and use a very small amount of resin.

5.0 Steam Generation

The basic function of a boiler is to generate steam from water by the input of heat. In this section, the fundamentals of steam and its production are described. They include boiling, properties of water, and the use of steam tables to calculate necessary parameters for boiler and steam circuit operation.

The technical information in this section is intended for more experienced users, as reference material for understanding boiler operations. First-time readers of this manual may choose to skip this section and return to it later for detailed information.

5.1 PRINCIPLES OF HEAT TRANSFER

The subject of heat transfer is introduced in Chapter 1. This section discusses heat transfer principles involved in the steam generation process.

Briefly, heat is generated by the burning of fossil fuel (coal, gas, oil), nuclear fuel (uranium fission), and byproduct fuels; and also by sunlight (solar generation), and electrical resistance heaters. The heat is transferred to water by a heat exchanger (fossil or solar), or by direct contact (nuclear or electrical resistance). In the fossil category, heat recovery steam generators (HRSGs) are a special case, where hot turbine exhaust gases are passed through a series of heat exchangers to extract heat value from the waste gas stream.

In fossil fuel boilers, the burning fuel creates a flow of hot gases and a radiant fireball. These gases and radiant energy impinge on tubes containing flowing water. Convection and pumping circulate the water through the boiler tube system, usually to a steam drum. Steam is produced in the boiler tubes, and is separated in the steam drum. The steam is then throttled to the proper pressure, and may be superheated as needed.

Feedwater is heated by extraction steam from the main steam in feedwater heat exchangers. Usually the water entering the boiler will be close to the boiling temperature of the water at the rated boiler pressure. The heat input to the boiler mainly goes into changing the phase from liquid to vapor (steam). Heat of vaporization is the biggest component of the heat input.

Heat is transferred at a rate given by the amount of energy reaching the external surface of the boiler tube by convection and radiation from the burning fuel. At each interface (air/steel, steel/water, etc.) there is a temperature differential, but the heat flux, energy per unit area per unit time, is constant. If this were not so, one of the interfaces would continuously heat up. In the case of insulating deposits, the heat transfer can be impaired, and tube overheating takes place. This can ultimately result in a catastrophic tube failure.

The heat transfer equation is:

$$Q = U\,A\,\Delta T \qquad (3\text{-}4)$$

where: Q = heat load, in BTU/hr

A = surface area, in ft^2
ΔT = temperature gradient, in degrees F per foot
U = heat transfer coefficient, in BTU/(hr-ft-°F)

Note: 1 BTU = the heat needed to raise 1 pound of water by 1 degree F at 72 degrees F.

The value of U is characteristic of the interface. There are separate values for the hot gas/tube OD surface, the tube ID surface/water film, the water film/bulk water, tube ID/deposits, and deposits/water film. These U coefficients are experimentally determined, and vary widely with conditions. Heat is transferred across each interface at the same rate. In order to achieve this equality, the temperature gradient will vary. A small heat transfer coefficient will produce a large temperature gradient to preserve the equality. Knowing the heat rate, the heat transfer coefficients, and one temperature (usually the bulk water temperature) one can calculate all the other temperatures.

The heat rate can be determined by the steam rate and boiler dimension data. It takes approximately 1000 BTU per pound of water to produce a pound of steam. The actual value can be obtained from steam tables, and will vary with the operating, or throttle pressure.

Example: A boiler at 300 psig produces 50,000 pph of saturated steam. The boiler tubes have an ID area of 150 square feet and area steel ¼ inch thick. The heat transfer coefficient of steel is about 150 BTU/sq. ft. – deg.F – HR. If we ignore the various film coefficients, what is the skin temperature on he O.D. surface?
First calculate the heat flux. At 300 psig, the heat of vaporization of water is 804 BTU/lb.
The heat flux is then:
Q/A = 804 x 50,000/150 = 268,000 BTU/sq. ft. – hr.
Next find the bulk water temperature. From steam tables, that value is 422 deg. F.
Now find the temperature gradient. T = Q?A x 1/U = 268,000/150 = 1786 deg.F/ft.
Next find the temperature rise across the ¼ inch tube wall. T = 1786 deg.F/ft x 0.208 ft. = 37 deg. F.
Finally add the temperature change to the bulk water. TOD = 422 + 37 = 459 deg. F.

In this calculation, we ignored the other interfaces, and also the differential surface area between the OD and the ID surfaces of the boiler tubes. We also ignored the fact that the side of the tubes facing the furnace receives most of the heat flux.

5.2 BOILING

5.2.1 Principles

Matter exits in three phases: solid, liquid and gas. Each phase has certain general properties. Solids occupy a definite volume and have a definite shape. Liquids have a definite volume but assume the shape of the container they are in. Gases have neither a definite volume or shape. They will expand to fill the entire volume they are contained in.

Forces hold atoms and molecules together, but the application of energy can overcome these forces. If enough energy is applied to a given solid, the atoms or molecules will vibrate strongly enough to break the forces holding them together in a specific arrangement. The solid melts. The molecules are still attracted to one another enough to prevent their total escape, so the volume is maintained, but the shape is not, as the molecules can freely move around. The addition of still more energy can overcome the remaining attractive forces, and the molecules are no longer bound together. They form a gas.

At first, the addition of energy only increases the temperature, but once the temperature of the phase change (solid → liquid, or Liquid → gas) is reached, further input of energy leads to the phase change with no change in temperature. Only when all the matter has changed phase, will further energy input increase the temperature. During a phase change, the system is said to be in equilibrium. Two, or all three phases are present.

5.2.2 Phase Equilibria

The Phase Rule governs how phases will achieve equilibrium. It is stated by the following formula:

$$f = c - p + 2 \qquad (3\text{-}5)$$

where: f = degrees of freedom.
c = number of components in the system.
p = number of phases present.

Consider pure water, with no dissolved solids and no gases present other than water vapor. The system has one component (water). If conditions are set so that three phases (solid, liquid and vapor) are present, then from equation (3-5), the degrees of freedom equals zero. That is, the system is invariant. If the temperature is changed, water will freeze or ice will melt. If the pressure is changed, water will evaporate or vapor will condense into water. This is called the triple point for water. For interest, the triple point of water is 32.0135 °F at a pressure of .006 atmospheres (0.088 psia). There is no other pressure/temperature point at which all three phases can co-exist because there are zero degrees of freedom.

Now consider the same system with only two phases present, liquid and vapor. From equation (3-5), f = 1 and the system is monovariant. Water and water vapor (saturated steam) have one degree of freedom. At any given temperature, the steam will have a definite pressure. That information is summarized in steam tables (section 5.3.6).

A single component in a single phase, like liquid water, has two degrees of freedom. The temperature and pressure can be independently changed without creating a new phase. However, once the phase boundary is reached and a new phase begins to form, then the degrees of freedom are reduced to one and the system is constrained to exist along a definite line on a pressure-temperature phase diagram. For the water/steam system, that line is the boiling point. The line describes the vapor pressure of the steam in equilibrium with the water. If the ambient pressure is equal to the vapor pressure, the water will boil.

5.2.3 The Boiling Process

Ordinarily, vapor escapes the liquid only at the surface. However, when the ambient pressure is less than or equal to the vapor pressure, then bubbles of gas will form anywhere in the liquid as long as the vapor pressure exceeds the combined force of the ambient pressure and the weight of the liquid column. A column of water 33 feet high exerts the same pressure as one atmosphere, or 14.7 pounds per square inch. So, for example, in order to boil water at the bottom of a 33 foot deep pool (at sea level), the temperature would have to at least equal the temperature at which water has a vapor pressure of two atmospheres, or 29.4 psi. According to the steam tables, that occurs at 250° F.

Boiling, under sub-critical conditions (defined in section 5.3.4) occurs in three stages: nucleation, coalescence, and disengagement:

- Nucleation is the process by which the first microscopic bubbles form. The hottest points in the system, usually the tube walls in a boiler, will be the location of this process. The microscopic bubbles will adhere to the walls by capillary forces.
- The micro-bubbles will begin to merge as they grow, and their boundaries begin to collide. This is coalescence.
- Once the bubble grows to a certain size, it will disengage from the tube surface, and boiling takes place. As the bubble grows, a smaller proportion of the surface area of the bubble remains in contact with the surface. Disengagement happens because as the bubble grows, the buoyancy force increases, and the adherent forces decrease.

5.2.4 Disengagement

This is the critical process for boiling in a boiler. The flow of the steam/water mixture is critical for good boiler operation. If it is not properly controlled, then steam blanketing can occur, and tube overheating and rapid failure can ensue.

Heat is transferred through the boiler tube walls to the liquid inside. As the water flows in the tubes to the steam drum, it becomes hotter. At some point, the boiling point is reached for the throttle (operating) pressure of the boiler. Bubbles begin to form on the surface. The bubbles collapse as they are cooled by contact with the cooler bulk water (called subcooled boiling). Further along, the entire bulk fluid reaches the boiling point for the operating pressure. Bubbles begin to form everywhere. This process is called nucleate boiling.

Eventually, the vapor production rate becomes so great that the steam forms a film at the internal (ID) surface of the tube. Steam insulates the tube wall. Heat transfer to the bulk fluid is greatly restricted, and the tube wall temperature rises rapidly. This point is known as critical heat flux, or departure from nucleate boiling, burnout or dryout.

Flow in the boiler tubes is critical at this point. If too low for the heat flux, then the tubes can overheat and fail. Good boiler design will result in decreased heat flux in this region, so that stable, or film boiling will occur. Heat is transferred to the liquid through a thin film of water vapor at the tube ID surface, but the rate of heat transfer is stable because the heat flux is lower in this region of the boiler than in the lower sections. Tube geometry and baffles are used to regulate the heat flux.

Bubbles of steam form in the bulk liquid, and the density decreases. Convective flow (or pump-assisted flow) moves the fluid along towards the steam drum, the bubbles reach the surface of the liquid and coalesce. Once the bubble size is great enough, buoyancy forces overcome surface tension and the bubbles break. The steam exits and fills the head space of the drum.

5.3 PROPERTIES OF WATER

In order to understand the physics of boiling, steam flow, and condensation it is necessary to understand the physical chemical properties of water. These include vapor pressure, density, heat of vaporization, and critical behavior.

5.3.1 Vapor Pressure

As previously explained (section 5.2.2), phases can coexist in equilibrium at a defined set of conditions. Water has a definite vapor pressure at a given temperature. In the bulk fluid, any water molecule has an equality of forces acting on it from all directions because only water molecules surround it. The water molecule moves freely through the fluid volume.

At the surface, however, these forces are not in balance. The attraction of water molecules for one another (through hydrogen bonding and Van der Waals attraction) occurs only on the liquid side of the interface. On the head space side, or vapor side of the interface, the attractive forces are much lower. This is the source of surface tension that holds the liquid together.

Occasionally, a molecule of water at the surface acquires enough energy to break free of the surface tension forces, and it passes into the vapor phase (evaporation). Occasionally, a molecule of water vapor collides with the surface, loses some energy to the bulk fluid, and becomes entrained in the water (condensation). At a given temperature, these two processes will come into equilibrium with each other. The rate of vaporization equals the rate of condensation. No further change in the amount of vapor in a given volume takes place. In a closed space at a fixed temperature, the vapor will achieve a stable pressure, the vapor pressure, of water.

The vapor pressure is characteristic of a given temperature. Steam tables (section 5.3.6) tabulate the vapor pressure of pure water for a range of temperatures. If the ambient pressure is equal to or less than the vapor pressure of water at that temperature then boiling will occur. The steam tables, then are a list of the boiling points of water at various pressures. These values are only true for pure water. The presence of dissolved substances will lower the vapor pressure at a given temperature, and the boiling point is raised. This is so because the vapor pressure lowering means that a higher temperature has to be reached in order for the vapor pressure to equal the ambient pressure.

5.3.2 Density

As the pressure increases, the density of the gas increases. If we approximate the gaseous behavior of steam by the Ideal Gas Law (Boyle's Law):

$$PV = nRT \tag{3-6}$$

where: P = pressure, in atmospheres.
V = volume.
n = the number of molecules (or moles) of the vapor.
R = the gas constant.
T = the absolute temperature.
ρ = steam density

In these terms, density is defined as n/V times the molecular weight (a constant for water at 18 grams per mole). From equation (3-6):

$$\rho = n/V = P/RT \tag{3-7}$$

Note that in equations (3-6) and (3-7), P is not the vapor pressure, which is a property of the water and the temperature, since there is no equilibrium between the two phases.

Since n/V = P/RT, clearly at a given temperature, as the pressure increases the density must also increase. This has consequences for steam flow.

As the pressure rises, the gas density increases. This means that a given diameter of steam pipe can contain more steam per unit length as the pressure increases. Assuming that viscosity doesn't change too much with temperature (a good approximation), then a steam line is more efficient at carrying steam as the pressure is raised. This is one important criteria when designing a steam distribution system.

If for example, a steam rate of 100,000 pounds per hour (lb/h) is needed, then the pipeline carrying the steam can be of lower diameter if the pressure is raised. However, the velocity will rise, and one must be careful not to exceed the critical velocity of the line, at which turbulent flow occurs. One must also consider the effect of velocity on valves, expansion joints and steam traps when considering the overall design of the system. The velocity of the steam will be given by

$$v = S/\rho A \tag{3-8}$$

Where v = velocity
S = steam flow rate

ρ = steam density
A = the pipe cross sectional area.

The velocity increases inversely proportionately with the steam density.

5.3.3 Heat of Vaporization

This quantity is often referred to as the enthalpy of vaporization. Enthalpy is tabulated in steam tables. Simply put, it is the amount of energy needed to convert a unit of water from the liquid state to the vapor state at the boiling point, without changing the temperature. All the energy input, or work, goes into overcoming the surface tension forces and transporting the water across the interface into the vapor state.

This quantity is often considered to be a constant, equal to about 1000 BTU per pound, but it does, in fact, vary with temperature.

In section 5.3.1 we saw that there are unbalanced forces at the interface, and that water molecules experience a net force pulling them into the liquid. In order to pull a molecule free of the surface, it must have an additional amount of energy sufficient to overcome the interior attraction. As the temperature rises, the liquid expands, the molecules move ever more rapidly, and the chemical bonds vibrate more rapidly and with greater amplitude.

The liquid expansion means that the molecules are farther apart, decreasing the forces between them. The more rapid motion also decreases the Van der Waals attraction forces because the molecules are in close contact for a shorter period of time. The increasing bond motion also lowers the hydrogen bonding attractive forces between the molecules. All of these factors act to lower the attraction of surface molecules to the interior, and so the energy needed to vaporize a molecule also decreases. The enthalpy of vaporization goes down as the temperature increases.

This effect has consequences for many steam calculations. It also affects the economics of boiler operations. It requires less energy to vaporize a pound of water at higher pressures, so that fuel costs per unit of steam decrease at higher pressures. This can be seen most effectively for supercritical steam, which has a zero heat of vaporization, as shown in Table 3-2.

TABLE 3-2 Enthalpy of Vaporization of Steam

Temperature, °F	Pressure, psia	Enthalpy of Vaporization, BTU/lb
74	.4155	1051.8
212	14.696	970.3
402	250	822.0
486	600	734.7
545	1000	648.7
636	2000	465.7
679	2700	314.5
705.47	3208.2	0

The last entry is for steam at the critical point. Note that the enthalpy of vaporization at this point is zero. The attractive forces at the surface no longer exist. Indeed there is no surface, because the vapor density and the liquid density are the same. In essence, there is only one phase at or above the critical pressure, and so there is no phase transition energy. This condition is discussed further in the following section.

5.3.4 Critical Point

As seen in Table 3-2 and Figure 3-16, the heat of vaporization disappears at 705.47° F, corresponding to a pressure of 3208.2 psia (to convert to gauge pressure, psig, simply subtract 14.7 psi from the psia value, since the gauge registers the difference between the steam pressure and the ambient pressure).

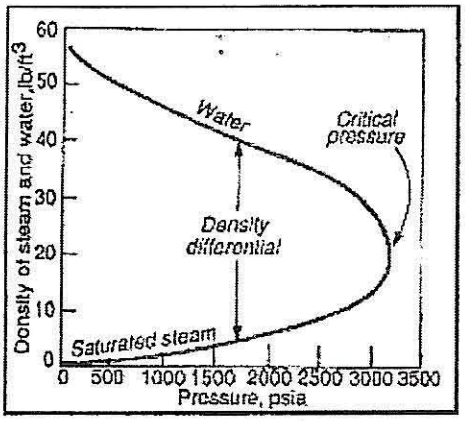


FIGURE 3-16
Density-Pressure Diagram for Water

In Figure 3-16, the density of water and steam are plotted vs pressure. As pressure (temperature) increases, the density of water decreases, and that of steam increases. At the critical pressure, the two densities are equal. There is only one phase. As there is no interface and no phase boundary, there is no phase change, and no enthalpy of vaporization. Above the critical pressure, only a single phase exists. The pressure at which the phases disappear is known as the critical pressure, and the corresponding temperature is the critical temperature. The density is known as the critical density.

5.3.5 Saturated vs Supersaturated Steam

At the phase boundary of water and steam, the two phases are in equilibrium. Any small change in pressure or temperature will cause the equilibrium to shift. If the pressure is decreased, additional water will become steam. If the pressure is increased, some of the steam will condense to water. If the temperature increases or decreases, a new vapor pressure is established.

That water/steam system is said to be saturated. The steam contains as much water vapor as it can hold. There is no moisture in the steam, but any cooling or increase in pressure will result in the formation of moisture (liquid water).

In steam lines this is important, since liquid water will promote corrosion. As long as there is no liquid phase present, the line cannot corrode. Saturated steam in the line will condense as it moves along the line and cools or loses energy in undergoing a process (expansion in a turbine for example, or air heating in a coil). At each stage, some of the steam will condense to form moisture. That moisture is called condensate, that can often be recovered to become part of the boiler feedwater (section 4.8).

If the saturated steam is further heated while not in contact with liquid water (as in a superheater) it will be raised above its saturation temperature. Now, some amount of cooling can take place without the formation of liquid. The steam line and handling equipment are protected from corrosion.

Another property change of superheated steam is that its density decreases. Since $n/V = P/RT$ (equation 3-7), clearly as the temperature increases at constant pressure, the density decreases. This means that the velocity in a superheated steam line will be greater for a given steam rate than it will be for saturated steam (section 5.3.2). As the degree of superheat increases, the steam line must be sized accordingly to prevent excessive velocities.

The enthalpy (heat content) of the superheated steam also increases with superheat temperature. This means that there is greater work potential per pound of superheated steam at a given pressure. In general, superheated steam is more efficient to use and cheaper to produce for a given amount of steam energy.

The degree of superheat is the temperature difference between the superheated steam temperature and the saturated steam temperature at the same pressure. For example, 600 psia steam has a saturation temperature of 486.2 ^{o}F. Raising the temperature to 600 ^{o}F adds 113.8 degrees of superheat. The enthalpy increases from 1203.7 BTU/lb to 1290.3 BTU/lb. Thus, 87 BTU/lb can be extracted from the superheated steam at 600 psia without creating any condensate. See sections 4.6 and 4.7 for more on this subject.

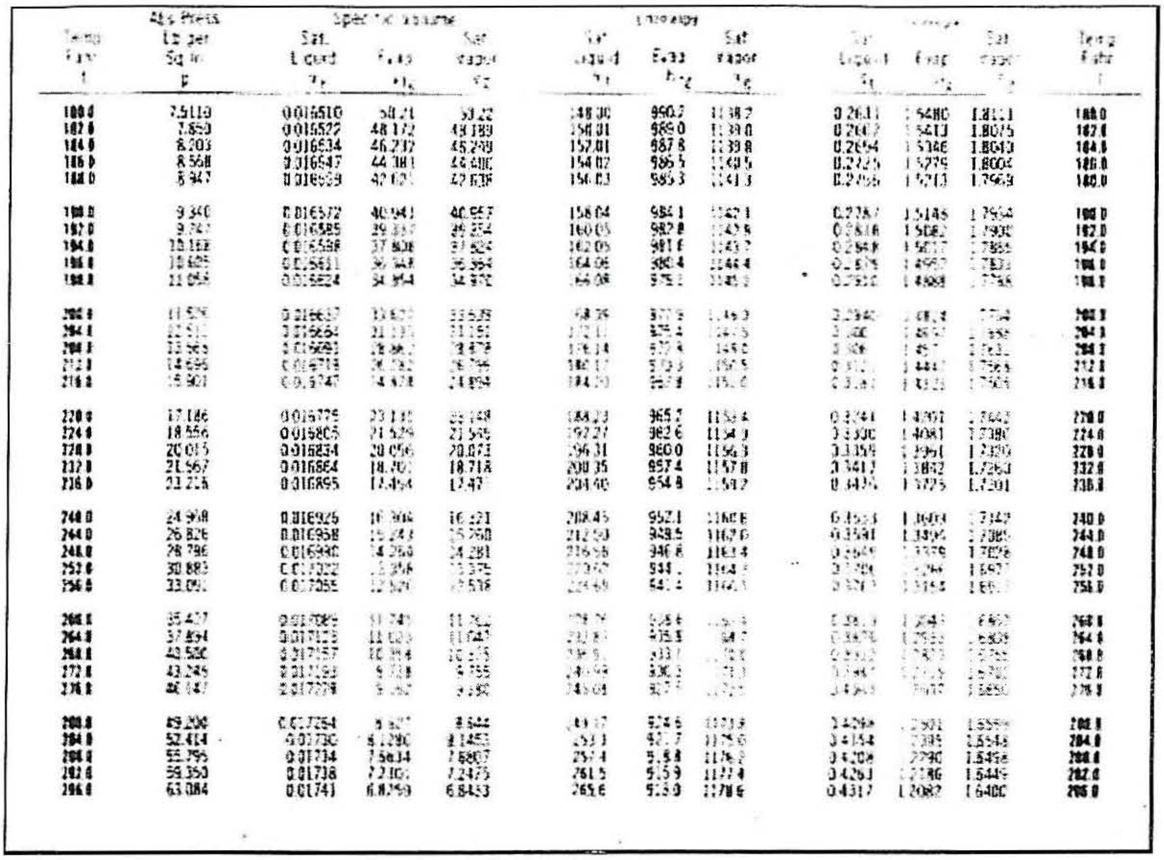
5.3.6 Steam Tables

Steam tables summarize all the important properties of steam. They show the saturation temperature of the steam at a given pressure, the enthalpies of the liquid and the steam, and the phase change or enthalpy of vaporization. They also tabulate information on the specific volumes (reciprocal of density) of the water and steam, and the phase change.

Another property included in the steam tables is the entropy of the liquid, steam, and phase change. Entropy is a thermodynamic property associated with the amount of "free" or available energy in a system. It is used mainly in the calculation of various properties around a cyclical operation, for example the amount of moisture contained in the steam after expansion in a turbine from one pressure to another. Entropy calculations are beyond the scope of this manual.

Steam tables are compiled for saturated and for superheated steam, and are readily available in textbooks and boiler manufacturers' literature. Table 3-3 is a portion of a saturated steam table.

TABLE 3-3
Saturated Steam Table



From Table 3-3, it is possible to calculate the heat input needed to produce a pound of saturated steam at a given pressure, and the density of the steam (reciprocal of the specific volume).

One looks up the temperature or the pressure of the steam, and then reads across to find the specific values of volume, enthalpy or entropy. Interpolation is possible by calculating the fraction of the interval.

> Example, if the temperature is 235° F, what is the pressure and total enthalpy of the steam?
>
> The Table contains entries for 232 and 2236° F. The desired temperature is ¾ of the way from 232 to 236° ((235-232)/(236-232)= ¾). The pressure is calculated by adding ¾ of the interval pressure from 232 to 236°F to the pressure at 232, or 21.567 + ¾(23.216-21.567)= 22.804 psia.
>
> The same holds true for the enthalpy. The enthalpy of saturated steam at 22.8 psia will be ¾(1159.2-1157.8) + 1157.8 = 1158.85 BTU/lb.

Superheated steam tables are partly shown in Table 3-4.

Table 3-4
Superheated Steam Table

Abs Press Lb/Sq In (Sat. Temp)		Sat Water	Sat Steam	Temperature — Degrees Fahrenheit 450	500	550	600	650	700	800	900	1000	1100	1200	1300	1400	1500
400 (444.60)	Sh			5.40	55.40	105.40	155.40	205.40	255.40	355.40	455.40	555.40	655.40	755.40	855.40	955.40	1055.40
	v	0.01934	1.1610	1.1738	1.2841	1.3836	1.4763	1.5646	1.6499	1.8151	1.9759	2.1339	2.2901	2.4450	2.5987	2.7515	2.9037
	h	424.17	1204.6	1208.8	1245.1	1277.5	1307.4	1335.9	1363.4	1417.0	1470.1	1523.3	1576.9	1631.2	1686.2	1741.9	1798.2
	s	0.6217	1.4847	1.4894	1.5282	1.5611	1.5901	1.6163	1.6405	1.6850	1.7255	1.7632	1.7988	1.8325	1.8647	1.8955	1.9250
420 (449.40)	Sh			.60	50.60	100.60	150.60	200.60	250.60	350.60	450.60	550.60	650.60	750.60	850.60	950.60	1050.60
	v	0.01942	1.1057	1.1071	1.2148	1.3113	1.4007	1.4856	1.5676	1.7258	1.8795	2.0304	2.1795	2.3273	2.4739	2.6196	2.7647
	h	429.56	1204.7	1205.2	1242.4	1275.4	1305.8	1334.5	1362.3	1416.2	1469.4	1522.7	1576.4	1630.8	1685.8	1741.6	1798.0
	s	0.6276	1.4802	1.4808	1.5206	1.5542	1.5835	1.6100	1.6345	1.6791	1.7197	1.7575	1.7932	1.8269	1.8591	1.8899	1.9195
440 (454.03)	Sh				45.97	95.97	145.97	195.97	245.97	345.97	445.97	545.97	645.97	745.97	845.97	945.97	1045.97
	v	0.01950	1.0554		1.1517	1.2454	1.3319	1.4138	1.4926	1.6445	1.7918	1.9363	2.0790	2.2203	2.3605	2.4998	2.6384
	h	434.74	1204.8		1239.7	1273.4	1304.2	1333.2	1361.1	1415.3	1468.7	1522.2	1575.9	1630.4	1685.5	1741.2	1797.7
	s	0.6332	1.4759		1.5132	1.5474	1.5772	1.6040	1.6286	1.6734	1.7142	1.7521	1.7878	1.8216	1.8538	1.8847	1.9143
460 (458.50)	Sh				41.50	91.50	141.50	191.50	241.50	341.50	441.50	541.50	641.50	741.50	841.50	941.50	1041.50
	v	0.01959	1.0092		1.0939	1.1852	1.2691	1.3482	1.4242	1.5703	1.7117	1.8504	1.9872	2.1226	2.2569	2.3903	2.5230
	h	439.83	1204.8		1236.9	1271.3	1302.5	1331.8	1360.0	1414.4	1468.0	1521.5	1575.4	1629.9	1685.1	1740.9	1797.4
	s	0.6387	1.4718		1.5060	1.5409	1.5711	1.5982	1.6230	1.6680	1.7089	1.7469	1.7825	1.8165	1.8488	1.8797	1.9093
480 (462.82)	Sh				37.18	87.18	137.18	187.18	237.18	337.18	437.18	537.18	637.18	737.18	837.18	937.18	1037.18
	v	0.01967	0.9668		1.0409	1.1300	1.2115	1.2881	1.3615	1.5023	1.6384	1.7716	1.9030	2.0330	2.1619	2.2900	2.4173
	h	444.75	1204.5		1234.1	1269.1	1300.8	1330.5	1358.8	1413.6	1467.3	1520.9	1574.9	1629.5	1684.7	1740.6	1797.2
	s	0.6439	1.4677		1.4990	1.5346	1.5652	1.5925	1.6175	1.6628	1.7038	1.7419	1.7777	1.8116	1.8439	1.8748	1.9045
500 (467.01)	Sh				32.99	82.99	132.99	182.99	232.99	332.99	432.99	532.99	632.99	732.99	832.99	932.99	1032.99
	v	0.01975	0.9276		0.9919	1.0791	1.1584	1.2327	1.3037	1.4397	1.5708	1.6992	1.8256	1.9507	2.0746	2.1977	2.3200
	h	449.52	1204.7		1231.2	1267.0	1299.1	1329.1	1357.7	1412.7	1466.6	1520.3	1574.4	1629.1	1684.4	1740.3	1796.9
	s	0.6490	1.4639		1.4921	1.5284	1.5595	1.5871	1.6123	1.6578	1.6990	1.7371	1.7730	1.8069	1.8393	1.8702	1.8998
520 (471.07)	Sh				28.93	78.93	128.93	178.93	228.93	328.93	428.93	528.93	628.93	728.93	828.93	928.93	1028.93
	v	0.01982	0.8914		0.9466	1.0321	1.1094	1.1816	1.2504	1.3819	1.5085	1.6323	1.7542	1.8746	1.9940	2.1125	2.2302
	h	454.18	1204.5		1228.3	1264.8	1297.4	1327.7	1356.5	1411.8	1465.9	1519.7	1573.9	1628.7	1684.0	1740.0	1796.7
	s	0.6540	1.4601		1.4853	1.5223	1.5539	1.5818	1.6072	1.6530	1.6943	1.7325	1.7684	1.8024	1.8348	1.8657	1.8954
540 (475.01)	Sh				24.99	74.99	124.99	174.99	224.99	324.99	424.99	524.99	624.99	724.99	824.99	924.99	1024.99
	v	0.01990	0.8577		0.9345	0.9884	1.0640	1.1342	1.2010	1.3284	1.4508	1.5704	1.6880	1.8042	1.9193	2.0336	2.1471
	h	458.71	1204.4		1225.3	1262.5	1295.7	1326.3	1355.3	1410.9	1465.1	1519.1	1573.4	1628.2	1683.6	1739.7	1796.4
	s	0.6587	1.4565		1.4786	1.5164	1.5485	1.5767	1.6023	1.6483	1.6897	1.7280	1.7640	1.7981	1.8305	1.8615	1.8911

In these Tables, read down to find the pressure of the steam (or the corresponding temperature of the saturated steam at that pressure). Then read across to find the values of specific volume (reciprocal of density), enthalpy or entropy of superheated steam at that pressure, but at elevated temperature.

The temperature difference between the superheated steam and the saturated steam is listed as ("Sh"), and is referred to as the "degrees of superheat." Again, interpolation is possible if specific sets of conditions are not tabulated.

Calculations are performed by reading data from the tables for two sets of conditions, and taking differences.

Example: how much heat energy is needed to provide 200 degrees of superheat to 1000 psia saturated steam?

The enthalpy of the saturated steam at 1000 psia is 1192.9 BTU/lb from the Table. Reading across to 200 degrees of superheat we find the values for 205 degrees. We must interpolate between 155.42 degrees and 205.42 degrees (700 and 750° F respectively). The interpolation factor is (200-155.42)/(750-700) = 0.8916. The enthalpy will be 1325.9 + .8916(1358.7-1325.9) = 1355.1. The enthalpy of 1000 psia saturated steam is 1191 BTU/lb, so we must supply (1355.1-1191.0) = 164.91 BTU/lb. If coal has about 12,000 BTU/lb and is about 50% efficient, then we must burn (164.91/12000)/.5 = .027 lb of coal to produce one pound of 200 degrees superheated steam at 1000 psia from a pound of the saturated steam.

6.0 Boiler Calculations

This section deals with common calculations needed to understand boiler operation, and for determining chemical feed rates. The main considerations are mass flows, steam, makeup, blowdown, feedwater, cycles of concentration and condensate return.

6.1 STEAM FLOW

This is the rate of steam production, S. It is a given for a boiler operating at a given pressure and fuel rate.

Heat requirements: Neglect extraction steam used for preheating the feedwater. Assume a final temperature for the feedwater. Look up the enthalpy of the saturated water at that temperature, and the enthalpy of the saturated steam at that pressure. Subtract to find the energy input required. Assume an efficiency for the boiler (supplied by the manufacturer) and a heat value for the fuel. From the fuel consumption, calculate the steam flow:

Example: Fuel oil with an average net useable heat value of 140,000 BTU/gal is burned at a rate of 860 gal per hour at 50% efficiency. How much steam is produced at 600 psia from a feedwater at 450 degrees F?
Energy value of oil = 140,000 BTU/gal x 880 gal/hour =$1.2\text{x}10^8$ BTU/hr
Energy available at 50% efficiency = $6\text{x}10^7$ BTU/hr.
Energy needed to produce one pound of 600 psia steam from 450°F water: From the tables:
h (sat'd. water at 450F) = 422 BTU/lb
h (sat'd steam at 600 psia) = 1203.6 BTU/lb
Energy input needed = (1203.6 - 422) = 781.6 BTU/lb.
Steam production rate = $6\text{x}10^7$ BTU/hr/ 781.6 BTU/lb = 76,750 lb/hr of steam.

6.2 MAKEUP

Makeup is the water needed to replace any water lost in the steam cycle. By mass balance:

$$FW = MU + CR = S + BD \qquad (3\text{-}9)$$

where FW = feedwater

MU = makeup
BD = blowdown
S = steam rate
CR = condensate returned.

Example: If a boiler steam rate is 40,000 pph, and there is 75% condensate returned, and the blowdown is 2000 pph, what is the makeup rate?
The condensate is .75x 40,000 = 30,000 pph
Total feedwater is S + BD = 40,000 + 2000 = 42,000 pph.
The makeup is FW - CR = 42,000 - 30,000 = 12,000 pph
The makeup water system must be sized for this rate of makeup production

6.3 CYCLES

Boiler cycles are the ratio of dissolved solids in the boiler to the dissolved solids in the feedwater entering the boiler. Just as in a cooling tower, periodic blowdown is needed to maintain an acceptable level of total dissolved solids in a boiler at a given pressure.

However, boiler chemicals are not normally injected into the feedwater, so the ratio calculation cannot be done by analytical methods. Also, alkalinity breakdown to caustic and volatile CO_2, and the precipitation of sparingly soluble salts, prevent such a direct measurement of boiler cycles.

Theoretically, cycles can be expressed by the relative flow rates of feedwater and blowdown. By mass balance:

$$C_{fw} M_{fw} = C_{bd} M_{bd}. \tag{3-10}$$

where C_{fw} = Concentration of a species in feedwater.
C_{bd} = Concentration of the same species in the blowdown.
M_{fw} and M_{bd} are the feedwater and blowdown flow rates.

If boiler cycles are defined theoretically as C_{bd}/C_{fw}, then it follows that boiler cycles, Cyc, are expressed as:

$$Cyc = M_{fw} / M_{BD}. \tag{3-11}$$

Boiler cycles are maintained by controlling blowdown, either continuously, intermittently, or both. This happens when, for example, sample lines run continuously, and intermittent surface and bottom blows are taken (once per shift, day, week, etc.).

6.4 BLOWDOWN

Blowdown is needed in all but supercritical once-through boilers or high pressure boilers on all-volatile treatments (AVT). Blowdown is used to control the buildup of feedwater impurities, boiler chemicals, and corrosion products in the boiler water. Blowdown is taken from both the boiler drum and the mud drum.

From mass balance:

$$FW = S + BD \tag{3-12}$$

$$FW/BD = Cyc \tag{3-13}$$

The percent blowdown is:

$$\%BD = (BD/FW) \times 100 \tag{3-14}$$

or 1/Cyc. From these it follows that:

$$BD = S / (Cyc-1) \tag{3-15}$$

Knowledge of blowdown rates is important, because non-volatile chemical feed to the boiler is based on blowdown rates. That is, chemicals are fed to the boiler to replace those lost by blowdown. Blowdown can be determined experimentally by chemical depletion. For boilers under 1500 psig, molybdate can be used as a tracer to determine a whole range of important boiler values.

Use of Molybdate: add a known quantity of a molybdate salt, such as sodium molybdate, $Na_2MoO_4.5H_2O$.(MW = 296, 54% as MoO_4). One pound will produce about 65 mg/L (as MoO_4) per 1000 gallons of boiler volume.

After addition, monitor the molybdate concentration for about 72 hours, taking samples about every 8 to 10 hours.

Plot the log of the concentration vs time on semi log graph paper. The equation is

$$\ln C = \ln C_o - BD \times t / V$$

where C is the concentration at time t, C_o is the initial concentration, BD is the blowdown in appropriate units , such as lb/hr, and V is the boiler operating liquid volume in the same units, i.e. pounds. You should get a straight line of negative slope.

Converting to base 10 logarithms on the semilog paper, one gets

$$\mathrm{Log}_{10} C = \mathrm{Log}_{10} C_o - BD \times t / 2.3V.$$

The slope of the line is -BD/2.3V, and the intercept is $\mathrm{Log}_{10}C_o$. From the intercept, one gets C_o ($=10^{intercept}$). From C_o and the amount of molybdate, calculate the boiler volume:

$$V \text{ (gal)} = \text{lb of sodium molybdate added} \times 6.47\times10^4 / \text{mg/L } MoO_4$$

From the known volume and slope, calculate the blowdown rate:

slope = -BD/2.3V, so that BD = -2.3 x V x slope.

6.5 CONDENSATE RETURN

Condensate is essentially pure water. As such it can be re-used for feedwater. It is usually mostly deaerated, and hot, so that its use saves on deaeration chemicals and fuel costs. Condensate return is covered in section 4.8.2.

6.6 SUMMARY OF MASS BALANCE FORMULAE

Make up requirements: MU = FW - CR = S + BD - CR = SxCyc / (Cyc- 1) - CR.
At high cycles (low blowdown) C ≅ C-1, MU ≅ S -CR, and if CR → 100%, then MU ≅ 0
Blowdown: BD = FW - S = S / (Cyc-1)
Feedwater: FW = S + BD = SxCyc/(Cyc - 1)
Makeup: FW = CR + MU, so that MU = FW - CR

6.7 ECONOMIC DATA

The equations in the previous section can be used to compute boiler operating costs. Chemicals are fed to the feedwater to adjust pH and to scavenge oxygen. Knowledge of the feedwater rate, chemical feed rate and chemical unit costs will allow the calculation of feedwater treatment costs.

Condensate return conserves makeup water. The size, operating and capital cost of the pretreatment train can be calculated from a knowledge of overall steam rates and condensate return.

Boiler chemicals are fed to the boiler based on blowdown and feedwater chemistry. Knowledge of makeup water chemistry and condensate return enables calculation of feedwater chemistry (hardness, silica, alkalinity and conductivity (see chapter 2). This sets the mg/L level of chemical treatment. From that, and the blowdown rate, one calculates the chemical cost of boiler treatment.

6.8 HEAT RECOVERY

Condensate is a source of heat: Condensate temperatures are on the order of 100 to 140° F. Makeup water is typically at ambient temperature of about 60 to 80F. Thus, about 40 to 120 BTU per pound of makeup water are saved per pound of condensate return.

Blowdown has heat value that can be used to preheat the feedwater, or it can be flashed to recover steam value and condensate.

6.9 EFFICIENCY

This is a complex subject. The most useful parameter is heat rate, defined as the cost of energy needed to produce a pound of usable steam. Because some steam is used to preheat water, operate turbine pumps, or deaerate feedwater, the overall heat rate is based on the main steam minus all extraction steam points. Minimizing blowdown, and maximizing condensate recovery through the use of chemical treatment, polishing, and flash tanks is also useful. However, this savings has to be balanced against the costs of the various processes. Often fuel costs are outweighed by chemical costs for treatment or polishing.

One of the most important factors in efficiency is condensate return. Other factors such as fuel costs, steam rate, design and maintenance of the boiler are not subject to the control of the operator or water treatment supplier. But the ability to recover and recycle condensate is closely tied to the chemical treatment of the boiler and preboiler systems.

Effective control of alkalinity in the steam, oxygen in the feedwater, and boiler deposits and corrosion all affect the quality of condensate.

Efficiency is calculated in different ways for different processes. The general calculation is of the form:

efficiency (%) = 100 x (energy input -energy output)/energy input

Example: Recovery Boiler

	Energy Input	**10^6 BTU/hr**
Total input 1668	Chemical heat in liquor	1575
	Sensible heat in liquor	41
	Sensible heat in input air	52
Total	Sensible heat in dry gas	89
	Moisture from air	2
	Moisture from hydrogen	93
	Moisture from liquor	126
	Reduction reactions	117
	Heat in smelt	55
	Radiation	5
output 520	Misc.	33

Efficiency (%) = 100 x (1668 - 520) / 1668 = 68.8%

7.0 Chemical Treatment

7.1 OVERVIEW

This section deals with specific chemical treatments. Type, purpose, and application are all discussed. The treatments are divided along the lines of preboiler and condensate systems, and the boiler itself. The preboiler system is usually treated with pH adjustment chemicals, amines, and oxygen control chemicals, called scavengers. The condensate system is treated with pH adjustment and corrosion control chemicals, volatile amines and filming amines. The boiler is treated with chemicals to control deposition of salts and corrosion products, buffering of pH, and dispersants.

The main objective in every case is to permit the safe and efficient operation of the boiler and steam handling system. Corrosion control aids in boiler cleanliness and prevention of equipment failures. Deposit control aids in the maintenance of good heat transfer, which translates into better efficiency and prevention of tube failures. In the condensate system, corrosion and deposit control are essential for recovery of condensate for re-use and to protect piping and equipment.

In discussing chemical treatment in boiler systems, the following terminology will be used:

- Pretreatment or external treatment:: Chemical and physical treatment of makeup water to prepare a consistent, satisfactory quality boiler feedwater. Pretreatment is covered in detail in chapter 2.
- Internal treatment: Chemical treatment of the boiler water to control mineral scaling, corrosion and general deposition in the boiler drums and boiler tubes.
- Condensate treatment: Chemical treatment of steam condensate, applied either in the steam lines or in the boiler, to control carbonic acid and dissolved oxygen corrosion in the condensate lines.

As a general rule, the higher the boiler pressure, the higher the quality of feedwater required. Therefore, the higher the pressure, the more chemical treatment is concentrated outside the boiler in water preparation (chapter 2), and the less internal boiler water treatment and condensate treatment is required.

Boilers are often classified by operating (throttle) pressure. These groupings are arbitrary, and there is much overlapping between groups, but for purposes of discussing chemical treatment the following groupings are convenient:

- Low pressure steaming boilers, operating below about 300 psig, that use untreated, or at best zeolite softened feedwater to make steam primarily for HVAC and humidification use. Feedwater may or may not be mechanically deaerated. These boilers require substantial internal treatment to maintain clean surfaces and prevent corrosion. Systems are simple, and precise control of chemical dosages and boiler operations is generally not required.

- Medium pressure boilers, between about 300 and 900 psig, are the workhorses of industry. These boilers are designed in many different ways, either packaged or field-erected (section 3.0) They provide steam for heating, power generation, transportation and process uses in a wide variety of commercial, institutional and industrial facilities. Feedwater is at least softened, and is normally demineralized and mechanically deaerated. Internal chemical treatment is required for alkalinity control to prevent boiler and condensate corrosion, and to prevent residual solids deposition. Dosages are lower than in low-pressure boilers, but since many of these boilers are quite large, usage can be substantial. Chemical reactions are complex and careful control is required. Many of these boilers are controlled by manual testing, but automatic control is preferred, especially in higher-pressure systems.
- High pressure boilers, between about 900 and 1200 psig, are used primarily for electric power generation, in large industrial plants and power stations. Feedwater is always demineralized and mechanically deaerated. Chemical dosages are low, primarily for alkalinity and corrosion control. Dosages are critical and control is almost always automated.
- Very high pressure boilers, from above 1200 psig to supercritical pressures (section 5.3.4) are found in large power generation stations. They require the highest possible purity feedwater but only very small amounts of chemical treatment.

Although not part of the above classification, hot water heating boilers are also an important segment of boiler water treatment. These units are similar to closed cooling systems. Chemical treatment of hot water heating boilers is discussed in this section and also in chapter 4 (cooling water).

This chapter is organized by chemical treatment (oxygen scavengers, internal treatments, condensate treatment, etc.). Then the treatments are classified by application to boilers in the pressure groupings above.

7.2 DISSOLVED OXYGEN CONTROL

Dissolved oxygen can lead to severe corrosion in the economizer section and in the boiler and condensate systems. In the feedwater system, it will contribute to metals transport into the boiler, where deposition can lead to under-deposit corrosion and long term overheating. Dissolved oxygen enters the system via makeup water, which is often air saturated, or leaks into condensers or through pump seals.

The most common effect of dissolved oxygen is to increase the corrosion of the feedwater heaters. Copper and iron oxides are formed which break loose and travel to the boiler. These metal oxides deposit on the hottest part of the boiler tubes and create insulating deposits. From the heat transfer discussion in section 5.1, such insulating deposits increase the temperature gradient needed to provide a constant heat flux. The temperature rises on the tube wall, and overheating may result. Over a long time, such overheating can lead to metal fatigue and failure. Copper deposits can also lead to galvanic corrosion of steel (see chapter 4).

Oxygen problems are especially severe where ammonia is present in significant quantities. In the presence of oxygen, ammonia is very corrosive to copper. Ammonia is used for feedwater pH adjustment. It can also be formed from the thermal breakdown of hydrazine:

$$3N_2H_4 = N_2 + 4NH_3 \qquad (3\text{-}16)$$

or from hydrothermal breakdown of organic amines:

$$R\text{-}NH_2 + H_2O = ROH + NH_3 \qquad (3\text{-}17)$$

Where R is a general organic group like $(HO)CH_2\text{-}CH_2\text{-}$ (ethanolamine).

Ammonia cannot attack copper metal itself. It reacts only with copper ions in the +2 oxidation state (cupric). In the feedwater loop, these will be in the form of cupric oxide (CuO) and hydroxide ($Cu(OH)_2$). The cupric state can only form if oxygen is present. So it is the combination of ammonia AND oxygen that is aggressive to copper alloys. If oxygen is kept low by mechanical and chemical means then ammonia will not be a problem for copper.

However, maintaining low oxygen levels can be a difficult task. Oxygen enters the system from makeup water, cooling water leaks, condensate storage tank equilibration with the atmosphere, and pump seal leaks. Systems that are frequently laid up or which fluctuate widely in load may be more susceptible to air inleakage.

In high pressure boilers, the economizer section is very susceptible to oxygen corrosion. It is the first predominantly steel surface where dissolved oxygen can directly attack the metal. If oxygen is present in the feedwater, heavy iron oxide deposits and deep hemispherical pits can form in the economizer tubes.

In the boiler itself, dissolved oxygen can lead to oxygen pitting and tube failure. Pits are hemispherical, with sharp edges, and often have caps of corrosion products.

7.2.1 Methods for Dissolved Oxygen Removal

Two methods are available for removing dissolved oxygen from boiler water and steam systems: mechanical stripping, or deaeration (see section 4.3); and chemical oxygen scavengers. Oxygen scavengers are reducing agents that react with even the very low levels of oxygen left in water by good deaeration. They are normally added to the storage section of the deaerator, to allow time for reaction before the feedwater reaches the boiler.

Low pressure boilers sometimes do not include mechanical deaerators. In these systems, oxygen scavengers are required to do the whole job of dissolved oxygen removal. Obviously, much larger dosages are required in this case.

Oxygen scavengers fall into several classes. These include sulfites and ascorbates (non-volatile), and hydrazines, hydroquinones, hydroxylamines and ketoximes (volatile). Each of these is discussed in the following sections.

7.2.2 Sulfite

Sulfites are used in lower pressure boilers. They are non-volatile, and so add dissolved solids to the boiler. Sulfites are very reactive, and can reduce oxygen to 5 ppb if used correctly.

The reaction of sulfite with oxygen can be written as:

$$2SO_3^{-2} + O_2 = 2SO_4^{-2} \qquad 3\text{-}18$$

Above 430 °F (350 psia) sulfite reacts with iron oxide:

$$3Fe_2O_3 + SO_3^{-2} = 2Fe_3O_4 + SO_4^{-2} \qquad 3\text{-}19$$

Fe_3O_4 is magnetite, an intermediate valence form of iron oxide that forms good protective oxide films (passive films) under boiler conditions (low or zero oxygen levels). However, sulfite is not considered to be a good passivating agent because it does not passivate low pressure boilers, where sulfite is most often used. Passivation can be accomplished in high pressure boilers, but high dosages of sulfite are needed.

Sulfite is commonly supplied as sodium sulfite, Na_2SO_3; sodium bisulfite, $NaHSO_3$; ammonium sulfite, $(NH_4)_2SO_3$; or sodium metabisulfite, $Na_2S_2O_5$. All of these species hydrolyze (react with water), and at the usual boiler water pH range, the sulfite ion, SO_3^{-2}, is the active species present.

Sodium sulfite can decompose to sulfur dioxide (SO_2) and hydrogen sulfide (H_2S) in the boiler. For this reason, the use of sulfites is limited to boilers under 900 psig. The feed rate should be as shown in Table 3-5. divided by the boiler cycles. Up to 600 psig, residuals of 5-50 mg/L can be used; above 600 psig, 5-20 mg/L is the safe limit. Avoid large overfeeds.

TABLE 3-5
Sulfite Feed Requirements

Chemical	Name	mg/L SO_3 per mg/L O_2
Na_2SO_3	Sodium sulfite	7.88
$NaHSO_3$	Sodium bisulfite	6.5
$(NH_4)_2SO_3$	Ammonium sulfite	7.25
$Na_2S_2O_5$	Sodium metabisulfite	5.94

Although sulfite reacts slowly with oxygen at room temperature, it reacts very quickly at elevated temperatures. Also, the presence of minute quantities of oxidizable metal ions like cobalt (Co^{+2}) will greatly accelerate the rate of reaction with oxygen. Many water treatment suppliers supply catalyzed sulfite products, usually containing cobalt.

As discussed above, sulfite does not passivate metal surfaces well and should not be used for this purpose.

7.2.3 Hydrazine

Hydrazine is a very common oxygen scavenger. It is an inorganic reducing agent of great power. However, the reaction rate of hydrazine with dissolved oxygen is slower than the sulfite reaction, For this reason, plus difficulties in handling, hydrazine is used most often in high pressure boilers.

The reaction of hydrazine with oxygen is:

$$N_2H_4 + O_2 = 2H_2O + N_2 \qquad (3\text{-}20)$$

At temperatures greater than 250 °F, hydrazine reacts with metal oxides:

$$6Fe_2O_3 + N_2H_4 = 4Fe_3O_4 + 2H_2O + N_2 \qquad (3\text{-}21)$$

$$4CuO + N_2H_4 = 2Cu_2O + 2H_2O + N_2 \qquad (3\text{-}22)$$

Ferric oxide is reduced to the familiar black, protective magnetite film (equation 3-21), and cupric oxide is reduce to red cuprous oxide (3-22). These reactions passivate, or protect the metal surfaces in the boiler, so that hydrazine is used as a passivating agent as well as an oxygen scavenger.

Hydrazine decomposes in boiler water at 400-600 °F (250-1500 psia):

$$3N_2H_4 = 4NH_3 + N_2 \qquad (3\text{-}23)$$

Feed rates of about 5 times stoichiometric are required for good oxygen scavenging. For every 1 mg/L of oxygen feed about 5 mg/L of hydrazine. The excess will break down to ammonia in the boiler (equation 3-23) and may cause problems in copper condensate systems unless they are air free. Hydrazine is typically supplied as a 35% solution in water.

Hydrazine is listed as a carcinogenic compound and must be handled with proper precautions.

7.2.4 Carbohydrazide

Carbohydrazide is a derivative of hydrazine. It reacts readily with oxygen:

$$(NH_2NH)_2C{=}O + 2O_2 = 2N_2 + 3H_2O + CO_2 \qquad (3\text{-}24)$$

Decomposition: carbohydrazide first breaks down to hydrazine and carbon dioxide, and then decomposes to ammonia and nitrogen.

Reduction of metal oxides:

$$(NH_2NH)_2C{=}O + 12Fe_2O_3 = 8Fe_3O_4 + 3H_2O + 2N_2 + CO_2 \qquad (3\text{-}25)$$

$$(NH_2NH)_2C{=}O + 8CuO = 4Cu_2O + 3H_2O + 2N_2 + CO_2 \qquad (3\text{-}26)$$

Thus, the passivating properties of carbohydrazide are similar to hydrazine. However, the produced carbon dioxide adds to the potential for acidic condensate, and must be taken into account.

The feed rate is the same as for hydrazine: about 2.5 times stoichiometric, or about 5.6 mg/L per mg/L of oxygen.

7.2.5 Hydroquinone

Hydroquinone is a powerful reducing agent (scavenger). Its reaction with oxygen is:

$$2C_6H_4(OH)_2 + O_2 = 2C_6H_4O_2 \text{ (benzoquinone)} + 2H_2O \qquad (3\text{-}27)$$

Hydroquinone is also a goof passivating agent for both steel and copper:

$$C_6H_4(OH)_2 + 3Fe_2O_3 = 2Fe_3O_4 + \text{misc. organic products} \qquad (3\text{-}28)$$

$$C_6H_4(OH)_2 + 2CuO \rightarrow Cu_2O + \text{mixed organic products} \qquad (3\text{-}29)$$

The feed rate of hydroquinone for oxygen scavenging is approximately 3 to 7 mg/L per 1 mg/L oxygen.

The oxidation product of hydroquinone, benzoquinone (equation 3-27) can also scavenge oxygen. Thus the stoichiometric relation does not fully apply.

Hydroquinone is more reactive than other oxygen scavengers, and scavenges effectively at temperatures below 180 °F.

Hydroquinone is very toxic, and must be handled in a well ventilated area. For this reason, it is rarely used in HVAC systems.

7.2.6 Diethylhydroxylamine (DEHA)

The hydroxylamines, mainly diethylhydroxylamine, DEHA, are also used effectively for oxygen control.

Reaction with oxygen:

$$4(C_2H_5)_2NOH + 9O_2 = 8CH_3COOH + 2N_2 + 6H_2O \qquad (3\text{-}30)$$

The reaction product, acetic acid, is neutralized to form acetate ions with hydroxide in the boiler.

Reactions with metal oxides:

$$\text{DEHA} + 6Fe_2O_3 = 4Fe_3O_4 + CH_3CH{=}NOH + CH_3CHO + H_2O \quad (3\text{-}31)$$

$$\text{DEHA} + 4CuO = 2Cu_2O + CH_3CH{=}NOH + CH_3CHO + H_2O \quad (3\text{-}32)$$

DEHA has passivating properties, as shown by (3-31) and (3-32), but it is less effective for that purpose than hydrazine and hydroquinone.

DEHA breaks down above 300 psig to form a small amount of ammonia plus organic acids and carbon dioxide.

The stoichiometric rate is 1.2 mg/L per mg/L O_2. Feed at 6 mg/L, a 5:1 stoichiometric excess.

DEHA is an amine, and is sometimes used to neutralize carbon dioxide (carbonic acid) in condensate, as well as to scavenge oxygen (section 7.4).

7.2.7 Methyethylketoxime (MEKO)

Methylethylketoxime (MEKO) is another scavenger, not as widely used.

Reaction with oxygen:

$$2CH_3(C_2H_5)C{=}NOH + O_2 = 2CH_3(C_2H_5)C{=}O + N_2O + H_2O \quad (3\text{-}33)$$

Reaction with metal oxides:

$$2MEKO + 6Fe_2O_3 = 2CH_3(C_2H_5)C{=}O + N_2O + H_2O + 4Fe_3O_4 \quad (3\text{-}34)$$

$$2MEKO + 4CuO \rightarrow 2\ CH_3(C_2H_5)C{=}O + N_2O + H_2O + 2Cu_2O \quad (3\text{-}35)$$

MEKO also breaks down to ammonia and organic acids above 1800 psig, and at lower pressures if a large excess is fed to the boiler.

Feed rate: the stoichiometric rate is 4.7 mg/L per mg/L O_2; feed normally at 5 times the stoichiometric rate.

7.2.8 Ascorbate/Erythorbate

Ascorbic acid (vitamin C) and erythorbic acid, an isomer of ascorbic acid, are organic, non-volatile, non-toxic oxygen scavengers useful up to about 1500 psig.

Reaction with oxygen:

$$NaC_6H_6O_6 + \tfrac{1}{2}O_2 = C_6H_5O_6 + NaOH + \text{complex organics} \quad (3\text{-}36)$$

Reduction of metal oxides:

$$NaC_6H_6O_6 + 3\ Fe_2O_3 = C_6H_5O_6 + 2Fe_3O_4 + NaOH \quad (3\text{-}37)$$

$$NaC_6H_6O_6 + 2CuO = C_6H_5O_6 + Cu_2O + NaOH \quad (3\text{-}38)$$

Feed rate: the stoichiometric rate is 12 mg/L active acid per mg/L O_2; feed at 5 times stoichiometric.

7.2.9 Handling of oxygen scavengers

Oxygen scavengers are fed to the downcomer or storage section of the deaerator. A stoichiometric amount based on feedwater is added, plus enough to give the required stoichiometric residual. Table 3-6 summarizes feed rates for the various scavengers.

TABLE 3-6

Oxygen Scavenger Feedrates

Oxygen Scavenger	Operating Pressure, psig	mg/L Active / mg/L Oxygen
Sulfite	0 to 600	6-8 +20-50 mg/L residual (see Table 3-5)
Sulfite	601 to 900	6-8 + 5-10 mg/L residual (see Table 3-5)
Hydrazine	600 to >2500	5
Carbohydrazide	600 to >2500	5-6
Hydroquinone	300 to >2500	3-7
DEHA	150 to 600	6
MEKO	300 to 1800	25
Ascorbate/erythorbate	150 to 1500	60

It is very important to remember that the data in Table 3-6 are guidelines only. Each system must be evaluated individually, and feed rates and residual requirements may vary. Oxygen scavengers must be selected for specific applications. Some scavengers may not be suitable due to handling problems, speed of reaction and plant process requirements.

Reactions of oxygen scavengers with dissolved oxygen are not instantaneous. Scavengers and oxygen may coexist in the boiler water, depending on temperatures and available reaction time. It is therefore essential to measure oxygen levels in the condensate and feed water to determine performance. Iron and copper levels should also be monitored.

Most oxygen pitting corrosion problems occur during boiler down time. Proper layup procedures are critically important. For layup, oxygen scavengers are fed to the boiler water as the boiler is being filled, to provide 100 to 500 mg/L active scavenger. Amines are also added for pH adjustment. See also section 10.2.3 in this chapter.

7.3 INTERNAL CHEMICAL TREATMENT: HARDNESS CONTROL PROGRAMS

Boiler internal treatments are designed to prevent deposition of sparingly soluble salts of hardness and silica that may be in the feedwater. The recommended limits of these and other substances in feedwater for various pressure ranges are discussed in section 7.6.

Internal treatments are also designed to prevent corrosion by a variety of means. Ordinarily, the hydrothermal reaction of iron with water will produce a stable, protective (passive) film of magnetite, Fe_3O_4, if the pH is controlled in the 9 to 11 range. Corrosion inhibiting programs are designed to maintain this pH by a buffering effect, or by the control of alkalinity breakdown in the boiler.

$$3Fe + H_2O = Fe_3O_4 + H_2 \quad \text{(Schikorr Reaction)} \qquad (3\text{-}39)$$

It is still vital to control oxygen levels with good deaeration and oxygen scavenging practice. Internal treatments cannot prevent unacceptable levels of corrosion in a boiler if oxygen levels are above 5 to 10 ppb in the boiler on a regular basis.

7.3.1 Carbonate Cycle

Unless the feedwater is demineralized and polished (demineralizer train, mixed bed polisher, or reverse osmosis/mixed bed polisher, see chapter 2) it will contain alkalinity. Alkalinity is defined as the capacity to neutralize hydrogen ions, H^+. Alkalinity should not be confused with "alkaline", which is a water condition where the pH is on the basic side of neutral (see chapter 1, section 6).

Although the definition of alkalinity is general, and can apply to any proton (hydrogen ion) acceptor, in boiler systems alkalinity is concerned mainly with carbonate.

Carbonate salts exist in water due to the dissolution of limestone by acidic waters. The carbonic acid so formed reacts with alkaline metals like sodium or potassium, to form carbonate salts. Carbonic acid, H_2CO_3, exists in three forms: free carbon dioxide (carbonic acid/water), bicarbonate (HCO_3^-), and carbonate (CO_3^{-2}). Carbonic acid equilibria, alkalinity and P and M alkalinity relationships are discussed in chapter 1, section 6 of this manual.

If either softened or raw water is used for makeup, alkalinity will be in the feedwater. For most feed waters, the alkalinity is almost completely in the form of bicarbonate. The bicarbonate breaks down in the boiler in a two-stage reaction:

$$2HCO_3^- = CO_2\uparrow + CO_3^{-2} + H_2O \quad \text{(essentially 100\% complete)} \quad (3\text{-}40)$$

$$CO_3^{-2} + H_2O = CO_2\uparrow + 2OH^- \quad \text{(about 80\% complete)} \qquad (3\text{-}41)$$

Taken together, two moles of bicarbonate will produce about 1.8 moles of carbon dioxide, or about 0.649 mg/L of CO_2 per mg/L of HCO_3^-. Converting bicarbonate to M alkalinity, about 0.79 mg/L of CO_2 are produced for every 1 mg/L of M alkalinity (as $CaCO_3$) in the boiler feedwater (see chapter 1).

The carbon dioxide passes completely into the steam, and dissolves in the condensed steam to form carbonic acid. This makes the condensate very acidic. Treatment with neutralizing amines is therefore needed to prevent acidic attack in condensate lines (section 7.4).

Left behind in the boiler is hydroxide ion (equation 3-41), making the boiler alkaline. This is desirable, since the pH range for optimum magnetite formation is about 9 to 11. High pH is also needed for effective formation of calcium phosphate precipitates, preventing scaling of the boiler by hardness. Also, precipitation of magnesium hydroxide and control of silica are dependent on maintaining the proper pH range.

For every mole of bicarbonate, about 0.8 moles of hydroxide are formed, or about 0.22 mg/L hydroxide for every 1 mg/L of bicarbonate. Put in terms of alkalinity expressed as mg/L $CaCO_3$, every one mg/L of M alkalinity in the feedwater will produce about 0.79 mg/L of P alkalinity expressed as $CaCO_3$.

Early treatments for low-pressure boilers made use of the carbonate cycle. Carbonate based treatment programs are the oldest of the currently popular methods of boiler internal treatment. A carbonate program uses alkalinity to combine with the feedwater hardness to form an insoluble precipitate under boiler conditions. This precipitate (suspended solids) is conditioned with a sludge conditioner (either polymers or tannins and lignins) to keep the suspended solids fluid or free flowing, and non-adherent. The sludge conditioner prevents the sludge from sticking to the boiler tubes, and eventually bakes on to form a adherent scale. Instead, the sludge will be removed through bottom blowdown of the boiler.

The carbonate based programs generate large amounts of sludge in the forms of calcium carbonate and magnesium hydroxide. With carbonate based programs, both hydroxide and carbonate alkalinity must be monitored and controlled to insure that both alkalinity forms are available to combine with any hardness present in the boiler. This means that boilers being treated with a carbonate cycle program must be blown down on a regular and frequent basis (once or twice every shift while the boiler is operating).

Carbonate cycle products are normally used in boilers with pressures under100 psi and without softeners included in the pretreatment of make-up water. The 100 psi limit reflects the fact that carbonate alkalinity is harder to maintain as boiler pressures increase due to the decomposition of carbonate at higher pressures. If the raw feed water is softened, carbonate treatment is used less frequently because phosphates, polymers, or phosphate/polymer programs will generally become more economical.

7.3.2 Phosphate Precipitation Programs

Phosphate precipitation programs are based on two important phenomena:

- The solubility of calcium phosphate is substantially less than calcium carbonate, so that phosphate added to boiler water will precipitate calcium hardness as calcium phosphate, thus preventing formation of calcium carbonate scale.
- The form of calcium phosphate that precipitates under boiler water conditions is hydroxyapatite, $Ca_5(OH)(PO_4)_3$. Hydroxyapatite forms a loose, fluffy precipitate that can be dispersed in the water with the aid of either

natural or synthetic polymers, and removed with blowdown. This effectively prevents mineral scale deposits from forming in the boiler.

Phosphate is added to the boiler to precipitate calcium hardness entering from the feedwater. Phosphate precipitation treatments are typically used in low and medium pressure boilers, up to 600 psi. Even with softened or demineralized feedwater, these boilers may contain hardness levels as high as 3 to 5 mg/L as $CaCO_3$ due to breakthrough from the water preparation train. Phosphate converts the hardness to hydroxyapatite:

$$5Ca^{+2} + 3PO_4^{-3} + OH^- = Ca_5(OH)(PO_4)_3 \qquad (3\text{-}42)$$

For every one mg/L of calcium as $CaCO_3$ in the feedwater, one mg/L of disodium phosphate (DSP, Na_2HPO_4) is needed to react with all the calcium. Some additional DSP should be added to produce a phosphate residual in the boiler. A typical residual would be from 5 to 30 mg/L as PO_4^{-3}. Since 1.49 mg/L of DSP contributes 1.0 mg/L PO_4^{-3}, the amount of DSP needed will be about 1.49 times the desired phosphate residual in the boiler. Taking boiler cycles into account, DSP fed to the feed water will be:

$$\text{FW DSP} = \text{FW Ca} + 1.5 \times \text{desired residual } PO_4^{-3}/\text{boiler cycles} \qquad (3\text{-}43)$$

Or, if fed directly to the boiler based on blowdown:

$$\text{DSP} = \text{FW Ca/cycles} + 1.5 \times \text{desired } PO_4^{-3} \text{ residual} \qquad (3\text{-}44)$$

If trisodium phosphate (TSP, Na_3PO_4) is used instead of DSP, then the corresponding TSP fed to the feed water will be:

$$\text{FW TSP} = \text{FW Ca} \times 1.15 + 1.7 \times \text{desired residual } PO_4^{-3}/\text{cycles} \qquad (3\text{-}45)$$

Or, if fed directly to the boiler based on blowdown:

$$\text{TSP} = \text{FW Ca} \times 1.15/\text{cycles} + 1.7 \times \text{desired } PO_4^{-3} \text{ residual} \qquad (3\text{-}46)$$

The values above are calculated based on the anhydrous forms of the phosphate salts. However, most of the phosphate salts come as hydrates. Table 3-7 details the addition rates of the various phosphates and Table 3-8 contains operating parameters for phosphate precipitation programs vs boiler pressure.

TABLE 3-7 Phosphate Salt Addition Parameters

Salt	Feedwater		Boiler (based on blowdown)	
	Ca	Residual	Ca	Residual
DSP	FW Ca	1.5 x target residual/cycles	FW Ca/cycles	1.5 x target
DSP.12H_2O	2.5x FW Ca	3.8 x target residual/cycles	2.5 x FW Ca/cycles	3.8 x target residual
TSP	FW Ca x 1.15	1.7 x target residual/cycles	1.15 x FW Ca/cycles	1.7 x target residual
TSP .12H_2O	FW Ca x 2.7	3.95 x target residual/cycles	2.7 x FW Ca/cycles	3.95 x target residual

TABLE 3-8
Phosphate Treatment Guidelines

Parameter	Operating pressure psig		
	0-300	300-600	600-1000
PO_4^{-3}	30-60	30-60	20-40
P –alkalinity	300-600	300-500	200-400
SiO_2	150	50	15
neutralized conductance	2500-3500	2000-2500	1000-1500

Phosphate-based treatment programs are generally most cost-effective when softened water is used as boiler makeup. As with carbonate cycle programs, sludge conditioners (polymers) are needed to disperse the calcium phosphate formed by the reaction of phosphate with hardness, and to condition magnesium silicate. A typical treatment polymer is a low molecular weight polyacrylic acid (PAA) or polymethacrylic acid (PMA). Phosphate programs generate less sludge than carbonate programs, but still require regular and frequent blowdown.

Boiler conductivity will adversely affect polymer dispersancy capabilities. Polymer levels need to be augmented in higher conductivity waters. Typical polymer addition levels are given in Table 3-9.

TABLE 3-9
Polymer Addition Parameters in Phosphate Programs

Boiler Hardness, mg/L as $CaCO_3$	Polymer Actives, mg/L
<10	10-20
10-30	20-40
30-60	40-60
CONDUCTIVITY < 2200 μs/CM	ABOVE
2200-5000	1.5 x ABOVE
5000-9000	2 x ABOVE
9000-15000	3 x ABOVE
>15000	4 x ABOVE

7.3.3 Use of Polyphosphates and Organic Phosphates in Boiler Water

Inorganic phosphate chemistry is discussed in chapters 1 and 4. Briefly, phosphate compounds are available as a series of orthophosphates, discussed in section 7.3.2 above, and as polymerized forms known as polyphosphates. Typical commercial polyphosphates include potassium pyrophosphate, sodium tripolyphosphate, and sodium hexametaphosphate. These names are empirical and do not necessarily describe the chemical structures of these compounds. Structures vary with method of manufacture.

The important thing is that all of these complex phosphates are polymers of orthophosphate, and when dissolved in water, all will eventually hydrolyze (revert) to orthophosphate. The reaction rate is temperature sensitive. At boiler water temperatures, reversion is rapid, so that all forms of phosphate quickly become orthophosphate in the boiler.

However, this does not mean that polyphosphates should not be used. There are two good reasons for using polyphosphates in boiler water formulations:

- Ease of formulation: Trisodium phosphate is very alkaline and not very soluble in water. Phosphoric acid and dihydrogen phosphate are very soluble but also very acid. These factors create difficult problems in formulating complex boiler water products. Most of these problems can be avoided by using polyphosphates, that are quite soluble and more nearly neutral in pH.
- Avoiding calcium phosphate scale: Products containing orthophosphates should never be added to a boiler feedwater line, because of the possibility of precipitating calcium phosphate scale in the line. The consequence of doing this could be rapid plugging of the line, with disastrous effects on boiler operations. This problem also is easily avoided by using polyphosphates in formulations.

These same statements hold true for organic phosphates (phosphonates) such as HEDP (hydroxyethylidenediphosphonic acid). Papers have been published touting the value of using HEDP in low-pressure boilers. The fact is, however, that the same results can be achieved by adding an equivalent amount of phosphate to the boiler as orthophosphate. HEDP may well have important value in formulations, but it should be considered as a source of orthophosphate in the boiler water.

7.3.4 Chelant Programs

Another strategy for hardness control in boiler water is to complex the hardness and solubilize it. Chelants act to form complexes, which are extremely stable because they form multiple attachment points to the hardness ions. They react stoichiometrically, like the phosphates. Unlike the phosphates, they do not form insoluble precipitates, but rather form soluble species.

$$Ca^{+2} + \text{chelant} \Leftrightarrow \text{complex} \tag{3-47}$$

$$K = [\text{complex}] / [Ca^{+}]\,[\text{chelant}] \tag{3-48}$$

The most common chelant is EDTA (ethylendiaminetetraacetic acid). Values for the complex ion formation constants are shown in Table 3-10. Equilibrium constants are explained in chapter 1.

Table 3-10.
Complexation Constants For EDTA

Ion	K
Ca	3.9×10^{10}
Mg	4.9×10^{8}
Fe^{+2}	2.1×10^{14}
Fe^{+3}	1×10^{25}
Cu^{+2}	6.3×10^{18}

The EDTA complex effectively reduces the concentration of the available hardness below its saturation value, so that calcium carbonate will not precipitate.

The stoichiometry is 1:1 on a molar basis. Since EDTA tetrasodium salt has a molecular weight of 380 and calcium carbonate has a molecular weight of 100, then 3.8 mg/L of EDTA will be needed for every 1 mg/L of hardness ion as $CaCO_3$. Commercially, EDTA sodium salt comes as a 38% solution. Therefore, 10 mg/L of solution will be needed for every 1 mg/L of hardness. This is an easy relationship to use. However, when planning a chelant-based boiler water treatment program, the question of free chelant residual must be considered very carefully. See section 7.3.5, below, for a discussion of chelant corrosion and free chelant residuals.

Chelant programs need to be closely monitored, and controlled. Feedwater hardness is critical. The boiler hardness will be the feedwater hardness x boiler cycles. Iron and copper can also be treated with chelants. The feedwater should be analyzed for soluble, or active iron and copper. This can be done by analyzing a micron filtered feedwater sample. For every one mg/L of iron, use 6.8 mg/L of chelant, or 17.9 mg/L of 38% chelant solution. For copper the corresponding values are 6 mg/L and 15.7 mg/L per mg/L of soluble feedwater copper. The chelant demand for iron and copper must be added to the hardness demand before calculating the residual.

Overall, chelant programs have the ability to maintain very clean boilers, since they are based on soluble rather than precipitation chemistry. However, because they require careful control and monitoring, they are best-used in boilers that operate under stable conditions with few changes, and where experienced operators are available that have boiler monitoring as part of their assigned duties.

For the reasons explained above and in the following section, chelant programs are not recommended in boilers operating below 600 psi. The clean boilers produced by these programs make them tempting in low-pressure systems. However, oxygen inleakage and hardness overruns from softeners are common problems in these systems. With chelant programs in place, the results can be serious failures and explosion hazards.

7.3.5 Chelant Corrosion and Free Chelant Residuals

In the complete absence of dissolved oxygen, EDTA and other chelants are not aggressive, and free residuals as high as 20 mg/L can easily be tolerated. However, dissolved oxygen, even in trace amounts, makes EDTA extremely corrosive. Chelant corrosion takes the form of deep, longitudinal gouges in the boiler tubes. The areas of attack are severely thinned, clean, and non-porous. The magnetite coating is removed, and bare metal is visible. Damage can occur very quickly if a substantial EDTA residual is present and dissolved oxygen should accidentally enter the boiler water.

The reason for this severe attack is that oxygen and chelant work cooperatively to attack steel. EDTA by itself is not corrosive. However, oxygen corrodes the steel surface and tries to form what would be a protective, passive layer of magnetite, Fe_3O_4. However, the EDTA chelates the iron ions as they are formed, takes them out of circulation and prevents magnetite formation. No passive film is allowed to form, and the oxygen continues to attack bare steel.

The response to this situation must be twofold:

- Never allow dissolved oxygen in the boiler. Never use a chelant program in a boiler that may, even occasionally, show a measurable free oxygen residual. If a consistent level of residual oxygen scavenger can be maintained, this will normally solve this problem, except in unusual circumstances.
- As insurance, do not use an unnecessarily large chelant residual. Any residual, even 1 mg/L above the expected calcium hardness level in the boiler water, will ensure that no calcium carbonate forms. Larger residuals are often used, to account for expected variability in calcium levels. This must be a site-specific judgment call. The best solution is to improve feedwater preparation and boiler operations so that hardness levels in the boiler water stay low and constant, and then use a low chelant residual.

7.3.6 All Polymer Programs

All polymer programs are used with waters containing sufficient natural alkalinity to raise the pH to 10 to 11. At that pH silica is rendered less volatile, magnesium will precipitate as the hydroxide, and calcium will form calcium carbonate.

Applications are generally limited to below about 1000 psig.

The treatment is based on dispersing the solids that will form in the boiler with polymers, and maintaining a high enough pH to passivate the metal surfaces and to minimize the volatility of silica. See Chapter 4 for an in-depth discussion of polymer dispersion and inhibition activity.

The main principle of all-polymer internal boiler water treatments is that polymers act in two ways in the boiler water:

- Like chelants, they complex with hardness ions so that the hardness does not precipitate. Polymers are not as powerful chelants as EDTA, so that the ratio of polymer to boiler water hardness must be carefully controlled. On the positive side, polymers do not prevent magnetite films from forming, so that the potential corrosion problem with EDTA does not exist with polymeric chelants.
- Polymers also act like threshold dispersants by adsorbing on micro-crystallites and distorting the crystal structure. This interferes with crystal growth and adsorption on walls. Polymeric dispersants, specifically selected to disperse iron oxides and calcium carbonate, keep deposits off the tube walls and maintain a loose sludge that can be removed with blowdown.

Polymers typically used are based on polyacrylic acid and polymaleic anhydride. Often copolymers of acrylic and maleic acids are used. For higher temperature applications, polymers incorporating polymethacrylic acid and sulfonated polymers are effective. Sulfonated styrene-maleic anhydride copolymers are common in these programs.

All-polymer programs can be used in boilers ranging from very low pressures up to about 1000 psig, but hey are only cost-effective if softened or demineralized makeup water is used. Performance of specific polymers varies. Applications above 1200 psig are feasible, but should be used only if the specific polymers have been tested for stability and performance at higher pressures. Limitations on all-polymer programs arise because:

- The polymers begin to thermally degrade at higher temperatures.
- The polymeric chelates, already less stable than the corresponding EDTA chelates, become even less stable with increasing temperature. At the same time, the solubility of calcium carbonate continues to decrease, so that above a specific temperature for each polymer, the chelation effect no longer prevents scale formation.
- Analytical tests for polymers are less reliable than for phosphate and carbonate. They can be very inaccurate if dissolved oxygen is present in the water.

All-polymer programs are compatible with most oxygen scavengers and neutralizing amines. Caustic can be added to supplement the natural alkalinity in the feedwater. Because polymer programs do not intentionally add insoluble ions, as do phosphate precipitation programs, boilers tend to stay cleaner.

As the pressure increases, polymer levels should increase and allowable hardness levels decrease. Table 3-11 details general application guidelines.

These are very general. Specific formulations will require a more conservative approach or allow for more relaxed guidelines. Polymer dosages should be based on total hardness plus iron demand in the system.

TABLE 3-11
All-Polymer Treatment Guidelines

Parameter	Pressure, psig		
	0-300	**301-600**	**601-900**
Polymer mg/L	15-30	30-60	60-90
P-alkalinity, mg/L $CaCO_3$	200-500	200-400	200-300
Silica (SiO_2)	<200	<50	<15

7.3.7 .Combination Programs

Chelants can be combined with phosphate to chelate some of the hardness, and precipitate the rest. In higher-pressure boilers where hardness levels are low, one can add up to 1 mg/L of chelant (2.6 mg/L of 38% solution). The remainder of the hardness can be precipitated by phosphate according to the guidelines in section 7.3.2. In this system, it is not necessary to carry a chelant residual, with its associated problems.

Chelants, polymer and phosphate can all be combined. The use of chelant with phosphate decreases the overall amount of polymer needed. For every 10% reduction in hardness treated by chelant, the polymer can be reduced by from 5 to 10 %. This program optimizes dosages of all three components, and avoids the need for a free chelant residual.

These programs are attractive where precipitation programs are needed at the high end of the medium pressure range. A major advantage is that because there is no need for a free chelant residual, the problem of chelant corrosion of steel is avoided.

7.3.8 Comparison of Hardness-Control Programs

The four precipitation chemistry internal boiler water treatment programs discussed in this section overlap. In most cases, more than one program will be suitable. The choice must be made on a site-specific basis, involving feedwater quality, boiler operating modes, operator availability and skills, and economic factors.

The following summary in Table 3-12 highlights the advantages and disadvantages of each program, as an aid in program selection. It is important to remember, however, that site-specific factors and individual water treatment supplier technology may override the general recommendations in this section.

TABLE 3–12

Comparison of Precipitation Programs

Program	Advantages	Disadvantages
Carbonate cycle	Simple and inexpensive. No added boiler solids. No special control or testing. Dosages not critical. Best in very low pressure boilers with little attention.	Can not tolerate high heat loads Boilers will be considered dirty. Not suitable for critical systems.
Phosphate precipitation	Most forgiving program. Tolerates variable feedwater, steam loads and cycles. Best in low to medium pressure boilers with some hardness.	Large amount of boiler sludge. Boilers will show some deposits Not suitable in critical systems that must be kept clean.
Chelant	Cleanest boilers. No added boiler solids. No boiler sludge. Best for critical systems and long runs in stable systems.	Requires monitoring & control by trained personnel. Not best with variable loads or feedwater quality. Danger of chelant corrosion if oxygen enters boiler.
All – polymer	Clean boilers. No added boiler solids. Minimum sludge, no deposits. Useful over wide pressure range, safe chemicals.	Requires monitoring & control by trained personnel. Will not tolerate variable loads or feedwater quality. Polymers degrade at high temp
Chelant – phosphate	Advantages of phosphate program with less sludge, no chelant residual. Avoids chelant corrosion,	Requires monitoring & control by trained personnel. Not best with variable loads or feedwater quality.
Chelant–phosphate–polymer	Optimized program – reduce phosphate & chelant dosage, no chelant residual. Avoids chelant corrosion.	Requires monitoring & control by trained personnel. Not best with variable loads or feedwater quality.

7.4 INTERNALCHEMICAL TREATMENT: ALKALINITY CONTROL

7.4.1 Coordinated Phosphate Programs

Boilers that use very high purity feedwater should have no need for precipitation-type internal treatment programs because there should be nothing to precipitate. Feedwater will be demineralized and mixed-bed quality, with conductivity approaching less than 0.5 µS/cm. This includes the high end of the medium pressure boiler range, and all high pressure and very high pressure boilers.

Chelant and all-polymer programs (sections 7.3.5 and 7.3.6) may be the treatments of choice in these boilers if the feedwater contains soluble iron (often carried in with returned condensate). EDTA and polymeric chelants form complex ions with the iron so that iron oxide deposits can not form.

Another widely-used approach in high purity feedwater boilers is alkalinity control. The basis of these programs is to buffer the boiler water in the pH range of 9 to 11 so that a protective magnetite film can form, following the Schikorr reaction (equation 3-39). A secondary function of the program is to buffer the buildup of acid or caustic under any deposits that exist in the boiler. Chemical buffers for pH control are explained in chapter 1.

Phosphoric acid (H_3PO_4) is a weak acid. It ionizes in water in a manner very similar to carbonic acid (chapter 1), to form three ionized species: dihydrogen phosphate ($H_2PO_4^-$), monohydrogen phosphate (HPO_4^{-2}), and orthophosphate (PO_4^{-3}). These forms distribute according to pH, in a manner similar to the carbonate species. The phosphate ion distribution vs pH is shown in Figure 3-17.

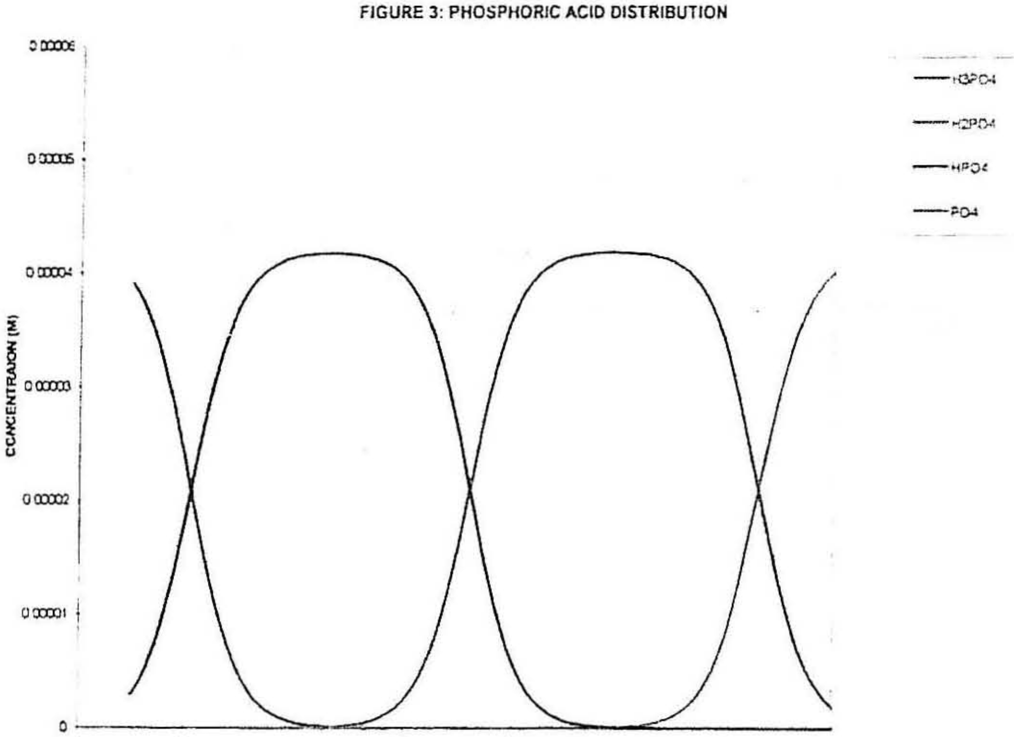


FIGURE 3-17
Distribution of Phosphate Species by pH

Note the similarity of Figure 3-17 to the carbonate species distribution graph in chapter 1, Figure 1-9.

In the critical pH region of 9 to 11 for magnetite formation, the predominant species are PO_4^{-3}, and HPO_4^{-2} (orthophosphate and monohydrogen phosphate). The sodium salts of these species are in the molar ratio of 3:1 and 2:1. In the pH 9 to 11 control range, then, the Na/PO_4^{-3} molar ratio will be from about 2.3:1 to about 2.5:1.

Besides the molar ratio, the absolute concentration of orthophosphate must also be considered. At the tube walls, and under any deposits that form, deposits, boiling will increase the local concentration of sodium phosphate species by several thousand fold. The buffer system must remain soluble to work. The bulk concentrations of the phosphate species must be controlled so that at these high concentrations they will remain soluble. In general, as the pressure increases (higher heat flux) the bulk concentration of the phosphate ion must decrease.

Under deposits, acids and caustic can concentrate to serious levels. At high acid concentrations, the hydrogen ion will act as a cathodic species to promote high rates of corrosion. The hydrogen gas formed in the cathodic reaction will react with carbon in the grain boundaries of carbon steel to form methane gas. The decarburization weakens the grain structure, and brittle failures can occur.

Caustic, concentrated up to 10,000 fold or more under deposits can produce pH levels above 14. Iron is very soluble in this pH range, and large, hemispherical gouges will form on the tube surface. The rate of attack is very high, and a tube failure can occur in a short time. This phenomenon is called caustic gouging.

The phosphate buffer system reacts with excess acid or caustic as follows:

$$H^+ + PO_4^{-3} = HPO_4^{-2} \qquad (3\text{-}49)$$

$$OH^- + HPO_4^{-2} = PO_4^{-3} + H_2O \qquad (3\text{-}50)$$

Figure 3-18 summarizes phosphate behavior in this program. This is the well known coordinated phosphate diagram. It has been published in many different forms, but program operating principles remain the same.

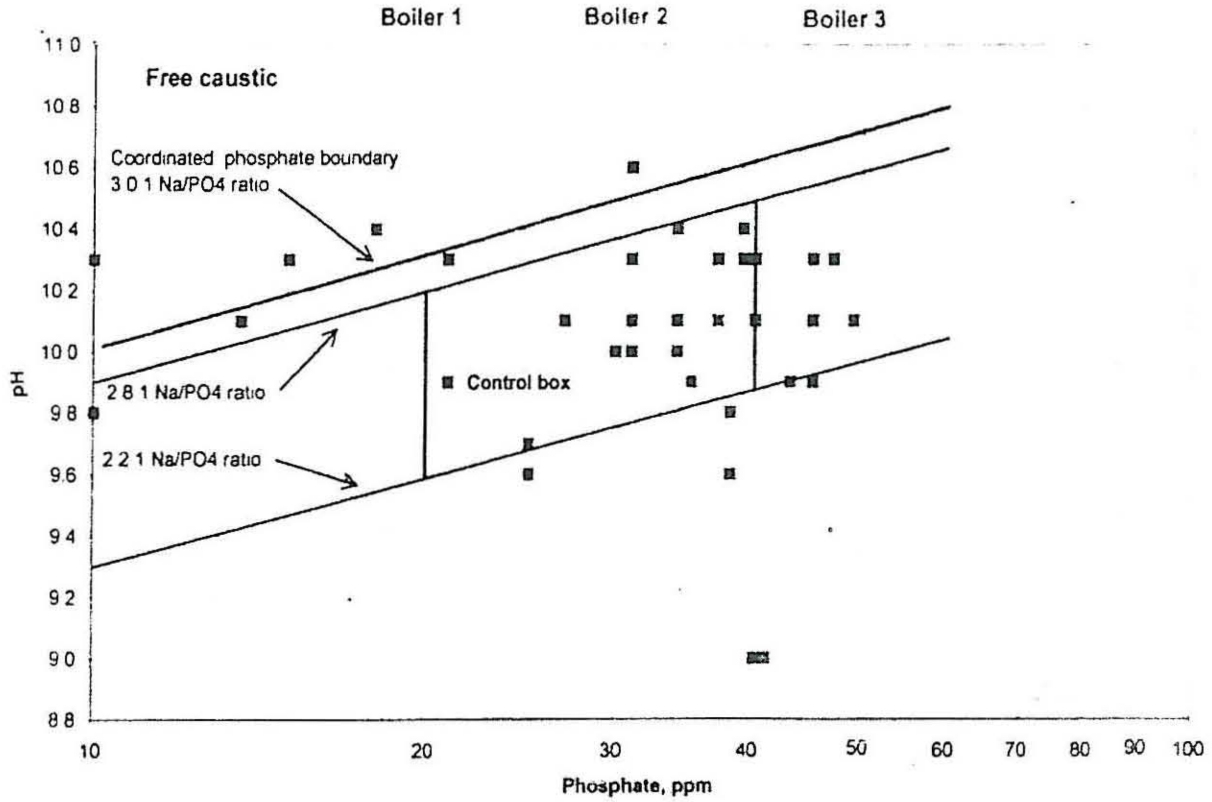


Figure 3-18. Coordinated Phosphate Control Diagram

The diagonal black and red lines in Figure 3-18 are lines of constant Na/PO_4^{-3} mole ratio. This is the main parameter. A good program is controlled between 2.2 and 2.8:1 mole ratio.

The objective of coordinated phosphate treatment is to buffer the pH so that there can be no free caustic in the boiler water. Localized boiling sometimes causes precipitation of boiler solids on tube surfaces. Water trapped beneath these deposits can become very concentrated (called caustic hideout). Avoiding free caustic in the water helps to ensure that caustic gouging of steel will not occur in these situations.

For this reason, the maximum boundary line in Figure 3-18 shows a Na:PO4 mole ratio of 3.0. This is the ratio in trisodium phosphate, Na_3PO_4. If the ratio is higher than 3, the excess sodium will come from caustic, NaOH. If the ratio is less than 3, there can be no free caustic because of the ionization equilibria in equations (3-49) and (3-50) and the phosphate ion distribution in Figure 3-17. Chapter 1 contains additional information on ionization equilibria.

Figure 3-18 shows that as boiler pressure increases, the control region moves to lower phosphate levels. This is to reduce the danger of precipitation from localized boiling at increased temperatures and heat fluxes. However, it is not conversely true that lower pressures require higher phosphate levels. It is just that more phosphate can be tolerated. The advantage to higher phosphate levels is that they buffer the pH better at higher levels of impurities.

Program control: A cooled sample of boiler water is analyzed for phosphate and pH. The coordinates of these two values are plotted as shown in Figure 3-18. If the point lies within the correct shaded box for the operating pressure, then the program is under control.

If the point lies outside the control box, corrective action is taken. Excessive phosphate is removed by blowdown. Too low a ratio is corrected by the addition of caustic or trisodium phosphate. The latter will increase both phosphate and sodium levels. Too high a ratio is controlled by addition of disodium phosphate or monosodium phosphate to consume sodium. Monosodium phosphate is not recommended, since overfeeds can depress the ratio to acidic pH levels.

The boiler pH should not be allowed to fall below 8.8. Therefore, at low phosphate levels, the mole ratio should be kept high to maintain adequate bulk water pH.

The data points in Figure 3-18 are from three boilers operating in parallel in a 900 psig cogeneration plant. Although most of the data points are within the control box, overall control of the coordinated phosphate program in this plant was poor. All three boilers operated at times below the minimum $Na:PO_4$ ratio, above the maximum phosphate level, and well into the free caustic range. This is not acceptable control, and over time, serious phosphate deposits, caustic gouging corrosion and boiler tube failures developed in this plant.

7.4.2 Hideout in Coordinated Phosphate Programs

Hideout is a phenomenon where phosphate levels decrease without apparent cause. The reverse process, hideout return, can also occur. Phosphate levels increase without apparent cause.

The reason for hideout or return is the precipitation of phosphate species at the boiler tube walls when the local concentration exceeds the solubility of sodium phosphate. Usually this is caused by hot spots or sudden increases in heat flux that raises the skin temperature sharply. Hideout return occurs when the precipitated deposits dissolve as temperatures drop.

In utility boilers, hideout occurs when unit load is increased, and return takes place when load is decreased. This is often associated with daily load cycles.

Hideout is a problem for coordinated phosphate programs because it makes program control difficult. Also, the phenomenon can result in mole ratios too high or too low for safe operation (>3.0:1 or < 2.2:1).

Hideout is generally incongruent. That is, the solid that forms does not have the same composition as the bulk solution. In that case, the solution chemistry will change. Not only phosphate levels, but mole ratios will change.

Attempts to prevent hideout by very closely controlling boiler water chemistry are usually fruitless and may make the problem worse. It is best to stay well within the control ranges in Figure 3-18, and to use as low a total phosphate level as possible while still maintaining good pH buffering in the water.

7.4.3 Congruent and Equilibrium Phosphate Programs

Generally below a Na/PO_4^{-3} mole ratio of 2.8:1, the precipitate that forms will have a mole ratio that is greater than the bulk solution mole ratio. The phosphate level will decrease, but the mole ratio in solution will decrease as well Overall the pH will decrease.

At a ratio of 2.8:1 the precipitation is congruent. Congruent precipitation means that the solid phase has the same composition as the solids in the bulk solution. At this point, the program control will not change with hideout or return. Coordinated phosphate programs operated at 2.8:1 mole ratio are called congruent phosphate programs.

Another congruent point is the 2.2:1 ratio. As hideout lowers the ratio, it will approach 2.2:1 and then stay there because the precipitation is congruent with the bulk water ratio. Coordinated phosphate programs can operate between these two congruent points.

To help avoid hideout related problems, equilibrium phosphate programs have been developed. In these programs, phosphate levels are allowed to decrease until load changes no longer produce hideout behavior. This establishes the equilibrium point. The main drawback to this program is that phosphate levels can be so low that buffer capacity is seriously degraded (section 7.4.1). Systems with a history of leaks into the boiler cannot operate well under equilibrium phosphate conditions.

The key points to remember are:

1. Coordinated phosphate programs are only applicable in high purity feedwater boilers.
2. Program control is based on phosphate and pH measurements, plotted on a diagram like Figure 3-18. Sodium measurements are not valid for program control, because not all sodium is involved in the buffer chemistry.

7.4.4 All Volatile Programs

All volatile treatment (AVT) is applicable only to very high-pressure boilers (>2400 psig) with very high purity feedwater and condensate polishing systems. Program control is based on using volatile amines and oxygen scavengers to maintain proper pH and oxygen levels in the feedwater and boiler. No nonvolatile solids are added to the boiler water.

There is no buffering capacity, so system leaks cannot be tolerated. Condensate polishing is required to handle any impurity ingress. Electric