utilities operating with sea water cooling systems cannot use AVT programs unless they are totally leak free (almost impossible), or have a very large polishing capacity.

Oxygen scavengers are covered in section 7.2. Only hydrazine can be used in AVT because it is volatile and breaks down only to safe species: $NH_3$, $N_2$, and $H_2O$. Species that contain carbon (carbohydrazide, hydroquinone, DEHA, MEKO) will break down to form carbonic acid in the condensate.

Likewise organic amines contribute carbon dioxide in the condensate. Consequently, most AVT programs use ammonia and hydrazine. Other amines, like morpholine and cyclohexylamine can be used, but condensate polishing is exhausted more frequently because of the carbonate loading.

The condensate polishers can be operated in the ammonia form instead of the hydrogen form. This prevents quick exhaustion or sodium breakthrough, but the tradeoff is poorer cation selectivity. This leads to higher sodium leakage rates.

High levels of ammonia can increase corrosion in the condensate system where there is copper based metallurgy, if air inleakage is significant.

Boiler pH is maintained in the range of 9.5 to 10.5. Dissolved oxygen must be controlled to less than 5 ppb.

### 7.4.5 Neutral Oxygen Treatment

Most boiler treatment programs are based on maintaining a reducing environment in the boiler. Mechanical deaeration and chemical oxygen scavenging are used to maintain oxygen levels in the low part per billion range. Under these conditions, if the pH is maintained in the range of 9 to 12, magnetite forms a dense protective film.

Neutral oxygen treatment is a new development pioneered in Europe for high pressure utility boilers operating with the best possible purity feedwater. If the pH is maintained in the neutral range of 7 to 8, and the oxygen is controlled in the range of 100 to 250 ppb, a very dense and thin, but highly protective magnetite film will form. Boilers treated on this program have not needed a chemical cleaning in over a decade of operation in many cases.

A variant, called combined oxygen treatment or combined water treatment (CWT) involves maintaining the pH at a slightly higher range of 8 to 8.5 with ammonia, and reducing the oxygen level to 75 to 150 ppb. Similar results are seen as for neutral oxygen treatment.

System requirements are as follows:

- All ferrous metallurgy, no copper alloys in the feedwater or condensate system.
- Full flow condensate polishing.

- Mechanical deaeration to 5 ppb.

Operationally, the feedwater is polished, deaerated, and then oxygenated under controlled conditions to the proper level. Program control is by dissolved oxygen measurements at the deaerator outlet and boiler feedwater, pH measurement in the feedwater and boiler, and cation conductivity in the condensate and the steam.

Control levels are: pH 7-8.5, specific conductivity consistent with ammonia treatment at pH 7-8.5, oxygen levels of 75 to 250 ppb at the economizer inlet, cation conductivity of <0.25 µS/cm in the main steam.

Combined water treatment systems have been used mainly in high pressure, field erected utility boilers, but smaller industrial boilers are beginning to use these programs successfully.

## 7.5 HOT WATER BOILER CHEMICAL TREATMENT

Most building hot water systems use city water. In some cases softened or partially softened water is used. Demineralized wafer is seldom used, but may be encountered in specialized cases such as pharmaceutical or microelectronics facilities, which may use the same water supply as for the process hot water heaters/boilers.

The use of city water (or well water) means that considerable amounts of sludge can form in these systems, much like home hot water heating systems. The sludge will accumulate in the heater, and to a lesser degree in the heat exchangers. Most treatments do not address sludge handling because these systems do not have mud drums or other convenient sludge removal systems. Sludge handling is usually done by periodic manual cleanings.

There are two modes of treatment usually involved. One is oxygen control, and the other is corrosion inhibition. Oxygen control focuses on the boiler-like environment, while corrosion inhibition approaches treat the system much like a closed loop cooling system. Each of these methods is discussed below. Chemical treatment of closed systems is also discussed in chapter 4.

### 7.5.1 Dissolved Oxygen Control

Sulfite is the treatment of choice (see section 7.2.2 for description of sulfite chemistry). Sodium sulfite is added as a liquid solution of up to 60 percent sodium sulfite. Sulfite is controlled to around 50 to 70 mg/L in the system. Addition is usually by a pot feeder.

Because of air leaks that can occur, sulfite control requires frequent monitoring. The monitoring is done by iodate-iodide titration, supplemented with direct dissolved oxygen measurements.

The titration method involves addition of potassium iodide-iodate solution to an acidified sample of the test water to which a starch indicator has been added. The test water will oxidize the iodide-iodate to iodine, which turns the indicator blue. The residual sulfite will reduce the iodine to iodide. When the blue color persists all the sulfite has been exhausted.

Sulfite treatment of hot water boiler systems should be undertaken only after very careful consideration. Because of the lower temperatures involved as compared to boiler water, the reaction of sulfite with dissolved oxygen is slow. Even with substantial sulfite residuals in the water, it is sometimes possible to detect low levels of dissolved oxygen. This is especially true when the system loses water that must be replaced with fresh oxygenated water.

In some cases, corrosion control treatment of the hot water is not possible because of use or discharge requirements. In such cases, sulfite is the treatment of choice. However, by far the majority of closed hot water systems are treated with corrosion inhibiting programs (section 7.5.2), rather than sulfite.

### 7.5.2 Corrosion Inhibition

Oxygen control is a means of corrosion inhibition by reducing the amount of corrodant. Corrosion inhibition here is meant as the introduction of chemicals which act to mitigate corrosion in the presence of the corrodant.

Building hot water heating systems can be treated like closed loop cooling systems because there is no change of phase, the water is generally not demineralized, and the system is closed. Because it is closed, certain types of inhibitors can be used which would be too expensive for use in open systems.

Inhibition choices include nitrite and molybdate. See also chapter 4 on closed cooling systems.

- Sodium nitrite is added as a liquid product. The target range when used alone is about 1000 to 1500 mg/L as nitrite in hot water systems. The pH of the system should be from 8.5 to 10, and preferably above 9.0. The pH is buffered in the proper range with sodium metaborate. If borate cannot be used, as in some nuclear plants, then add caustic to adjust pH.

  Testing is done by typical wet chemical methods for nitrite. The most common test is based on acidic ferrous sulfate. The ferrous ion reduces $NO_2^-$ to NO, which then forms a colored complex with excess ferrous ion.

  Because nitrite can decompose, it must be tested on a regular basis, and supplemented as needed. It can decompose to ammonia or nitrate, depending on conditions. It is useful to monitor nitrate or ammonia levels if nitrite levels regularly decrease. This will permit the assessment of what is causing the decomposition. Most nitrite will be lost via reaction with iron corrosion products or by slow oxidation if air can get into the system. Also, there can be some losses due to leaks.

  Microbiological degradation of nitrite is not common in hot water systems.

Nitrite programs cannot be combined with sulfite due to the reaction in which nitrite oxidizes sulfite to sulfate.

- Molybdate treatment of hot water closed systems is based on the inhibiting power of molybdate at high concentrations, especially for localized corrosion.

  When molybdate alone is used for hot water corrosion inhibition, the concentration should be at least 500 mg/L as $MoO_4$. The pH should be between 8.5 and 10, as for nitrite programs.

Molybdate is sensitive to chloride and sulfate levels. Typically, the molybdate level should be greater than the sum of these two ions, but not less than about 250 mg/L. If one or both of chloride or sulfate are high molybdate should be at least 250 mg/L above the sum of the two ions.

Blends of sodium molybdate and sodium nitrite are sometimes used to lower the total chemical dosage requirement. For example, with 150 mg/L molybdate as $MoO_4$, 500 mg/L nitrite as $NO_2$ is sufficient to provide good corrosion control.

Control is by testing for molybdate and nitrite. Again, nitrite may have to be supplemented, and molybdate may be needed if the system leaks significantly. The control pH range is 8.50 to 10.

### 7.5.3 Monitoring Hot Water Systems

Hot water boiler system performance is best monitored by inspections, coupons and pipe spools. Coupons should be used judiciously because water is lost from the system, and oxygen is added, every time the coupon rack is opened.

Pipe spools are placed in the main circulation with a bypass. The pipe spool is cleaned and weighed. After exposure it is removed, inspected for corrosion and fouling, cleaned and weighed, and then replaced.

Corrosion can be monitored as discussed in section 8.3.2. Iron monitoring is not reliable since many of these systems are old, and have copious amounts of iron oxide scale, which can occasionally slough off.

## 7.6 BOILER WATER CHEMISTRY LIMITS

Boiler chemistry control involves both the feedwater and the boiler section. The feedwater becomes the boiler water after it is chemically treated and cycled up. This section deals with the rationale for the various chemistry limits. The ASME consensus limits for boiler water chemistry are shown in Table 3-13. Table 14 summarizes operating guidelines for low and medium pressure firetube and watertube boilers.

## Table 3-13
## ASME Consensus Boiler Operating Guidelines

**SUGGESTED WATER CHEMISTRY LIMITS**
**INDUSTRIAL WATERTUBE, HIGH DUTY,**
**PRIMARY FUEL FIRED, DRUM TYPE**

Makeup water percentage: Up to 100% of feedwater
Conditions: Includes superheater, turbine drives, or process restriction on steam purity
Saturated steam purity target: See tabulated values below.

Makeup water percentage: Up to 100% of feedwatcr
Conditions: Includes superheater, turbine drives, or process restriction on steam purity
Saturated steam purity target: See tabulated values below.

| Drum Operating Pressure (1) (11) | psig 0-300 (MPa) (0-2 07) | 301-450 (2.08-3.10) | 451-600 (3.11-4.14) | 601 750 (4.15-5.17) | 751-900 (5.18 6.21) | 901-1000 (6.22-6.89) | 1001-1500 (6.90-10.34) | 1501-2000 (10.35-13.79) |
|---|---|---|---|---|---|---|---|---|
| **Feedwater (7)** | | | | | | | | |
| Dissolved oxygen ppm (mg/l) $O_2$ measured before chemical oxygen scavenger addition (8) | <0.007 | <0.007 | <0.007 | <0.007 | <0.007 | <0.007 | <0.007 | <0.007 |
| Total iron ppm (mg/l) Fe | ≤0.1 | ≤0.05 | ≤0.03 | ≤0.025 | ≤0.02 | ≤0.02 | ≤0.01 | ≤0.01 |
| Total copper ppm (mg/l) Cu | ≤0.05 | ≤0.025 | ≤0.02 | ≤0.02 | ≤0.015 | ≤0.01 | ≤0.01 | ≤0.01 |
| Total hardness ppm (mg/l)* | ≤0.3 | ≤0.3 | ≤0.2 | ≤0.2 | ≤0.1 | ≤0.05 | ND | ND |
| pH @ 25°C | 8.3 10.0 | 8.3 10.0 | 8.3-10.0 | 8.3 10.0 | 8.3 10.0 | 8.8-9.6 | 8.8-9.6 | 8.8 9.6 |
| Chemicals for preboiler system protection | NS | NS | NS | NS | NS | VAM | VAM | VAM |
| Nonvolatile TOC ppm (mg/l) C (6) | <1 | <1 | <0.5 | <0.5 | <0.5 | <0.2 | <0.2 | <0.2 |
| Oily matter ppm (mg/l) | <1 | <1 | <0.5 | <0.5 | <0.5 | <0.2 | <0.2 | <0.2 |
| **Boiler Water** | | | | | | | | |
| Silica ppm (mg/l $SiO_2$ | ≤150 | ≤90 | ≤40 | ≤30 | ≤20 | ≤8 | ≤2 | ≤1 |
| Total alkalinity ppm (mg/l)* | <350(3) | <300(3) | <250(3) | <200(3) | <150(3) | <100(3) | NS(4) | NS(4) |
| Free OH alkalinity ppm (mg/l)* (2) | NS | NS | NS | NS | NS | NS | ND(4) | ND(4) |
| Specific conductance (12) µmhos/cm (µS/cm) 25°C without neutralization | 5400-1100(6) | 4600-900(5) | 3800-800(5) | 1500 300(5) | 1200 200(5) | 1000 200(5) | ≤150 | ≤80 |
| **Total Dissolved Solids in Steam (9)** | | | | | | | | |
| TDS (maximum) ppm (mg/l) | 1.0 0.2 | 1.0 0.2 | 1.0 0.2 | 0.5 0.1 | 0.5 0.1 | 0.5 0.1 | 0.1 | 0.1 |

*as $CaCO_3$
NS - not specified
ND = not detectable
VAM = Use only volatile alkaline materials upstream of attemperation water source. (10)

### Table 3-14
### Summary Operating Guidelines for Low and Medium Pressure Boilers

| | | Firetube | Watertube | |
|---|---|---|---|---|
| **Feedwater** | **Units** | **0-300 psi** | **0-300 psi** | **301-600 psi** |
| Dissolved oxygen | mg/L | <0.007 | <0.007 | <0.007 |
| Total iron | mg/L | <0.10 | <0.10 | <0.05 |
| Tota; copper | mg/L | <0.05 | <0.05 | <0.035 |
| Total hardness | mg/l. $CaCO_3$ | <1.0 | <0.5 | <0.3 |
| pH range | pH units | 8.3-10.5 | 8.3-10.5 | 8.3-10.5 |
| Nonvolatile TOC | mg/L | <10 | <1 | <1 |
| Oily matter | mg/L | <1 | <1 | <1 |
| **Boiler Water** | | | | |
| Silica | mg/L $SiO_2$ | <150 | <150 | <90 |
| Total alkalinity | mg/L $CaCO_3$ | <700 | <1000 | <850 |
| Free OH alkalinity | mg/L $CaCO_3$ | Not spec. | Not spec. | Not spec. |
| Unneutralized conductivity | µS/cm | <7000 | <7000 | <5500 |

### 7.6.1 Alkalinity

Alkalinity breaks down in the boiler to form carbon dioxide, hydroxide ions, and a small amount of carbonate ion. Carbonate is not critical, since a phosphate or chelant program can prevent calcium carbonate scaling. The hydroxide is important in adjusting pH to the proper range for precipitating programs to work.

Calcium phosphate forms best above a pH of 10, where the phosphate ion predominates. Similarly, magnesium hydroxide forms above pH 10 . In order to achieve the proper pH range, the hydroxide alkalinity needs to be in the range of 200 to 500 mg/L as $CaCO_3$. The main control parameter is 2P-M (see chapter 1).

To control the program, the boiler water M and P alkalinity are measured, and 2P-M calculated. This value is the hydroxide alkalinity expressed as equivalent $CaCO_3$. A hydroxide alkalinity of 200 mg/L as $CaCO_3$ is an approximate pH of 11.5. At that pH, phosphate is efficient at precipitating calcium hardness, magnesium will precipitate as $Mg(OH)_2$, and silica will be soluble as $SiO_3^{-2}$ ion. This is the basis for control of phosphate precipitation programs (section 7.3.2).

Often it is necessary to add caustic to achieve the desired pH range if there is not enough natural alkalinity in the feedwater. This is also desirable form the condensate standpoint, since less carbon dioxide will be formed and pass over into the steam. This reduces the need for neutralizing amines.

### 7.6.2 Silica

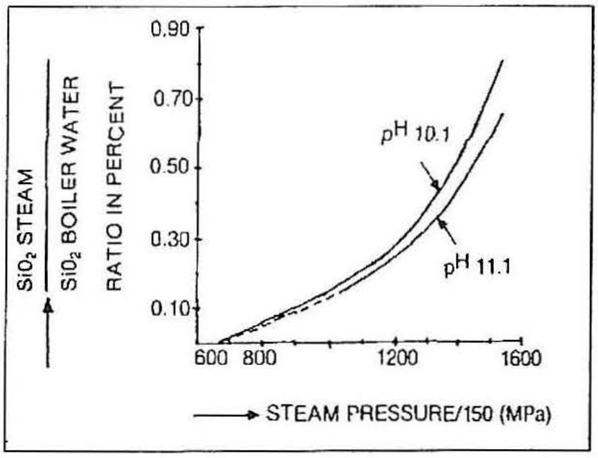
Silica is a volatile substance. It is generally considered that no more than 20 ppb of silica in the steam is permissible for the protection of turbines and other downstream elements. Allowed boiler water silica levels in turbine-quality steam are based on the volatility of silica as a function of temperature (Figure 3-19 and Table 3-15). As temperature (pressure) increases, the volatility of silica also increases. For that reason, the allowable limit of silica in the boiler decreases with increasing pressure so as to remain below the 20 ppb limit in the steam. By maintaining the pH high, most of the silica will be in the soluble silicate form. This minimizes the volatility of silica by restricting the concentration of the volatile $SiO_2$ form.

**TABLE 3-15**
**Solubility of Silica vs pH**

| pH | Solubility of amorphous $SiO_2$ (mg/L) at 77 F |
|---|---|
| 6 - 8 | 120 |
| 9 | 138 |
| 9.5 | 180 |
| 10 | 310 |
| 10.6 | 876 |

Silica in the steam often spikes at a pressure of about 1500 psig. At that point, silica-containing dust and dirt solubilize and begin to volatilize as $SiO_2$.

**Figure 3-19**
**Volatility of Silica vs Pressure**



### 7.6.3 Magnesium Hydroxide

Magnesium does not precipitate well as the carbonate or the phosphate. The control of magnesium is effected by pH control to a pH of >11 to precipitate $Mg(OH)_2$. If magnesium is not well controlled, it can form precipitates with silica, which are hard to remove.

Ordinarily, magnesium is not specifically tested. If the feedwater is suspected of having a high level of magnesium, steps should be taken to remove it by partial or full flow softening of the makeup water. The actual limits will vary due to boiler cycles and silica content.

## 7.7 CONDENSATE TREATMENT

Condensate is not usually pure. Various substances carry over physically or by volatilization in the boiler. When the steam condenses, many of these substances will dissolve in the condensate. Often, they impart objectionable properties to the condensate. Particulates and ionic species can be removed by condensate polishing, which is both a filtration process and an ion exchange process (chapter 2).

The main substance to be chemically treated in the condensate is carbon dioxide. Carbon dioxide is formed by the breakdown of carbonate alkalinity in the boiler. Being very volatile, most of it passes into the steam, and then forms carbonic acid in the condensate. The pH of the condensate can be depressed to very low levels, often below 3, because the carbon dioxide is not in equilibrium with the atmosphere, where the limiting pH is about 5.8.

Carbonate alkalinity can be removed by dealkalization and decarbonation in the pretreatment train (chapter 2), but in most medium and low-pressure systems, this is not done. To prevent the resulting acidic corrosion in the condensate lines, the carbon dioxide must be neutralized. This is done by adding neutralizing amines to the feedwater. Amines adjust the feedwater pH to a range of 8.8 to 9.2, which is optimum for a mixed metallurgy system. Passing into the boiler, amines distribute into the steam, and condense with the steam and carbon dioxide.

There are three important factors to be aware of with neutralizing amines:

- Basicity
- Neutralizing capacity
- Distribution ratio

### 7.7.1 Basicity

The general reaction of amines with water is:

$$RNH_2 + H_2O = RNH_3^+ + OH^- \qquad (3\text{-}51)$$

The base hydrolysis constant for amines (chapter 1) is defined as:

$$K_b = [RNH_3^+]\,[OH^-] / [RNH_2] \qquad (3\text{-}52)$$

The greater the value for $K_b$ the more basic is the amine. Basicity relates to the ability of the amine to raise the pH of neutralized water. On a molar basis, an amine with a larger value of $K_b$ will raise the pH of pure water higher than will an amine of lower $K_b$.

Tables 3-16 and 3-17, and Figure 3-20, present the pH of pure water as adjusted by the indicated amount of several volatile neutralizing amines. Note that higher basicity doesn't always translate into higher pH. The molecular weight also plays a role since this is on a mg/L basis, not a molar basis. Had the Table been computed for equimolar concentrations, then the highest $K_b$ would produce the highest pH.

## Table 3-16
## pH Adjustment Capacity of Amines pH vs Amine Concentration

| | CYCLO | DEAE | MOPA | MORPH | DMPA | DEA | MEA | NH3 |
|---|---|---|---|---|---|---|---|---|
| | pH | | | | | | | |
| mg/L | | | | | | | | |
| 0.2 | 8.32 | 8.25 | 8.36 | 8.21 | 8.29 | 8.23 | 8.49 | 8.91 |
| 0.5 | 8.71 | 8.62 | 8.74 | 8.48 | 8.65 | 8.54 | 8.84 | 9.20 |
| 1 | 9.00 | 8.89 | 9.01 | 8.67 | 8.91 | 8.75 | 9.08 | 9.40 |
| 2 | 9.29 | 9.15 | 9.28 | 8.85 | 9.16 | 8.96 | 9.31 | 9.58 |
| 3 | 9.46 | 9.30 | 9.43 | 8.95 | 9.29 | 9.07 | 9.43 | 9.68 |
| 4 | 9.57 | 9.40 | 9.53 | 9.02 | 9.39 | 9.14 | 9.51 | 9.75 |
| 5 | 9.66 | 9.47 | 9.61 | 9.08 | 9.45 | 9.20 | 9.58 | 9.81 |
| 6 | 9.73 | 9.53 | 9.67 | 9.12 | 9.51 | 9.25 | 9.63 | 9.85 |
| 7 | 9.79 | 9.58 | 9.72 | 9.16 | 9.56 | 9.29 | 9.67 | 9.89 |
| 8 | 9.84 | 9.62 | 9.76 | 9.19 | 9.59 | 9.32 | 9.71 | 9.92 |
| 9 | 9.89 | 9.66 | 9.80 | 9.22 | 9.63 | 9.35 | 9.74 | 9.95 |
| 10 | 9.93 | 9.69 | 9.83 | 9.24 | 9.66 | 9.38 | 9.77 | 9.97 |
| 11 | 9.96 | 9.72 | 9.86 | 9.27 | 9.69 | 9.40 | 9.79 | 10.00 |
| 12 | 10.00 | 9.75 | 9.89 | 9.29 | 9.71 | 9.42 | 9.81 | 10.02 |
| 13 | 10.03 | 9.77 | 9.91 | 9.30 | 9.73 | 9.44 | 9.83 | 10.04 |
| 14 | 10.05 | 9.79 | 9.93 | 9.32 | 9.75 | 9.46 | 9.85 | 10.05 |
| 15 | 10.08 | 9.81 | 9.95 | 9.34 | 9.77 | 9.48 | 9.87 | 10.07 |

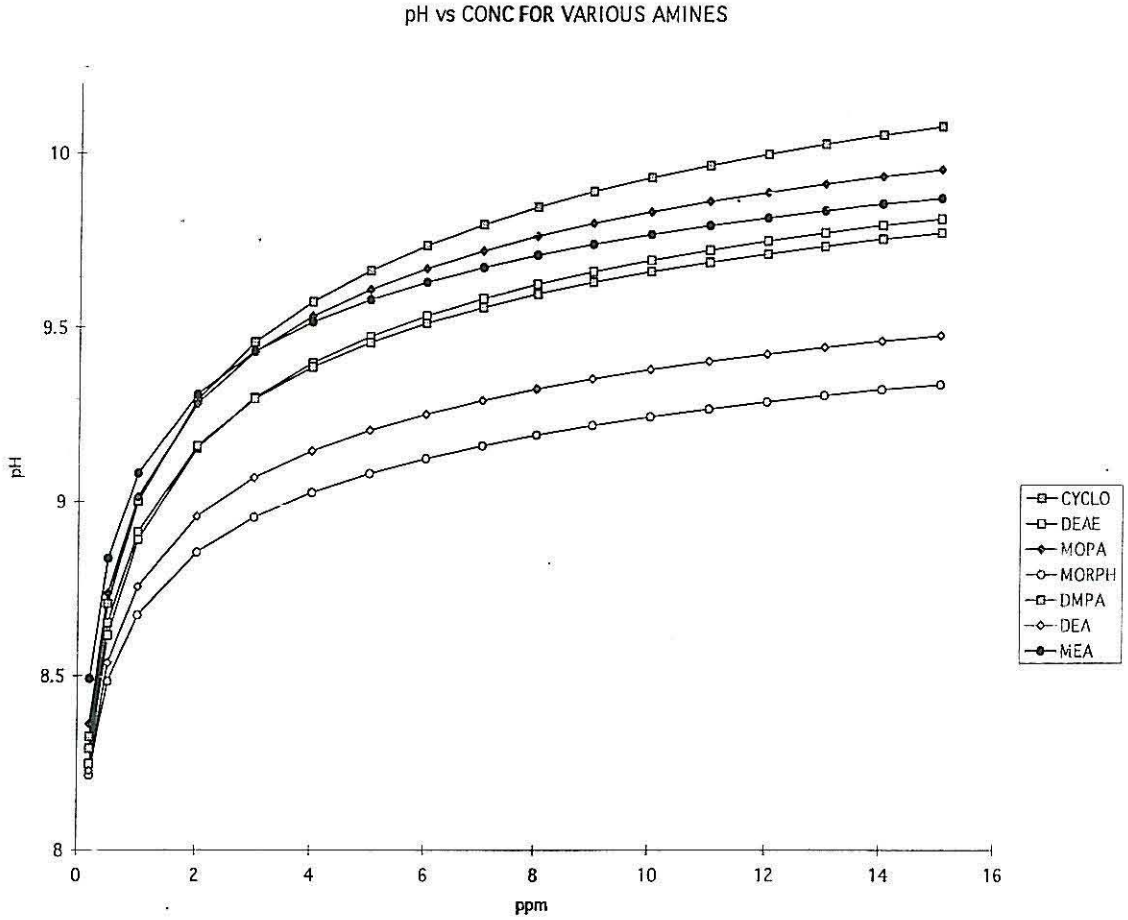
In Table 3-16:

CYCLO = cyclohexylamine
DEAE = diethylaminoethanol
MOPA = methoxypropylamine
MORPH = morpholine
DMPA = dimethylpropylamine
DEA = diethanolamine
MEA = monoethanolamine
NH3 = ammonia

## Table 3-17
## pH Adjustment by Amines: Amine Concentration vs pH

| | CYCLO | DEAE | MOPA | MORPH | DMPA | DEA | MEA | NH3 |
|---|---|---|---|---|---|---|---|---|
| | | | | | | | | |
| PH | mg/L | | | | | | | |
| 7.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 7.10 | 0.00 | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 7.20 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.00 |
| 7.30 | 0.01 | 0.02 | 0.01 | 0.01 | 0.02 | 0.02 | 0.01 | 0.00 |
| 7.40 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.01 | 0.00 |
| 7.50 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.02 | 0.00 |
| 7.60 | 0.04 | 0.04 | 0.03 | 0.04 | 0.04 | 0.04 | 0.02 | 0.01 |
| 7.70 | 0.05 | 0.06 | 0.04 | 0.05 | 0.05 | 0.05 | 0.03 | 0.01 |
| 7.80 | 0.06 | 0.07 | 0.06 | 0.06 | 0.06 | 0.07 | 0.04 | 0.01 |
| 7.90 | 0.08 | 0.09 | 0.07 | 0.09 | 0.08 | 0.09 | 0.05 | 0.01 |
| 8.00 | 0.10 | 0.12 | 0.09 | 0.11 | 0.10 | 0.12 | 0.06 | 0.02 |
| 8.10 | 0.12 | 0.15 | 0.11 | 0.15 | 0.13 | 0.15 | 0.08 | 0.02 |
| 8.20 | 0.16 | 0.19 | 0.14 | 0.21 | 0.17 | 0.20 | 0.10 | 0.03 |
| 8.30 | 0.20 | 0.24 | 0.18 | 0.28 | 0.22 | 0.26 | 0.13 | 0.04 |
| 8.40 | 0.25 | 0.30 | 0.23 | 0.39 | 0.27 | 0.35 | 0.16 | 0.05 |
| 8.50 | 0.32 | 0.39 | 0.29 | 0.56 | 0.35 | 0.46 | 0.21 | 0.06 |
| 8.60 | 0.40 | 0.49 | 0.37 | 0.79 | 0.45 | 0.63 | 0.27 | 0.08 |
| 8.70 | 0.50 | 0.63 | 0.47 | 1.14 | 0.58 | 0.86 | 0.35 | 0.11 |
| 8.80 | 0.63 | 0.81 | 0.60 | 1.67 | 0.75 | 1.19 | 0.46 | 0.14 |
| 8.90 | 0.80 | 1.04 | 0.76 | 2.46 | 0.98 | 1.67 | 0.60 | 0.19 |
| 9.00 | 1.01 | 1.35 | 0.98 | 3.68 | 1.29 | 2.38 | 0.80 | 0.26 |
| 9.10 | 1.28 | 1.75 | 1.26 | 5.54 | 1.70 | 3.43 | 1.07 | 0.36 |
| 9.20 | 1.63 | 2.30 | 1.63 | 8.43 | 2.28 | 5.00 | 1.45 | 0.51 |
| 9.30 | 2.06 | 3.04 | 2.12 | 12.91 | 3.08 | 7.39 | 1.98 | 0.72 |
| 9.40 | 2.63 | 4.06 | 2.79 | 19.89 | 4.21 | 11.02 | 2.73 | 1.02 |
| 9.50 | 3.36 | 5.47 | 3.69 | 30.82 | 5.83 | 16.61 | 3.84 | 1.48 |
| 9.60 | 4.30 | 7.47 | 4.93 | 47.94 | 8.18 | 25.25 | 5.45 | 2.17 |
| 9.70 | 5.53 | 10.32 | 6.65 | 74.85 | 11.63 | 38.65 | 7.85 | 3.22 |
| 9.80 | 7.14 | 14.44 | 9.09 | 117.22 | 16.75 | 59.54 | 11.44 | 4.83 |
| 9.90 | 9.28 | 20.48 | 12.57 | 183.99 | 24.43 | 92.20 | 16.87 | 7.31 |
| 10.00 | 12.15 | 29.43 | 17.63 | 289.34 | 36.05 | 143.41 | 25.16 | 11.14 |
| 10.10 | 16.03 | 42.83 | 25.03 | 455.74 | 53.78 | 223.87 | 37.89 | 17.11 |
| 10.20 | 21.34 | 63.07 | 36.02 | 718.74 | 81.01 | 350.50 | 57.55 | 26.42 |
| 10.30 | 28.71 | 93.92 | 52.49 | 1134.63 | 123.06 | 550.08 | 88.06 | 40.99 |
| 10.40 | 39.06 | 141.24 | 77.41 | 1792.60 | 188.34 | 864.99 | 135.60 | 63.86 |
| 10.50 | 53.81 | 214.27 | 115.40 | 2833.96 | 290.07 | 1362.32 | 209.91 | 99.82 |
| 10.60 | 75.07 | 327.54 | 173.72 | 4482.56 | 449.12 | 2148.30 | 326.40 | 156.45 |
| 10.70 | 106.13 | 503.93 | 263.78 | 7093.09 | 698.43 | 3391.21 | 509.40 | 245.75 |
| 10.80 | 152.04 | 779.56 | 403.52 | 11227.58 | 1090.11 | 5357.55 | 797.38 | 386.72 |

**Figure 3-20**
**pH Behavior of Amines in Pure Water**



## 7.7.2 Neutralizing Capacity

This parameter relates to the capacity of the amine to neutralize $CO_2$. The neutralizing reaction is:

$$RNH_2 + H_2CO_3 = RNH_3^+ + HCO_3^- \qquad (3\text{-}53)$$

The reaction is stoichiometric. The lower the molecular weight of the amine, the greater the neutralizing capacity. It has nothing to do with the basicity of the amine. Generally, the more alkalinity in the feedwater, the greater amount of neutralizing amine of any type will be needed.

## 7.7.3 Volatile Amines and Distribution Ratios

Volatile amines (neutralizing amines) follow the steam into the distribution system. The distribution ratio (DR) is a measure of the volatility of the amine (equation 3-54). It describes the ability of the amine to carry over into the steam where it can neutralize $CO_2$ in the condensate. Since amines are fed to the feedwater for pH control, they must then volatilize and pass into the steam to neutralize the condensate. The selection of amine has to be balanced by a consideration of feedwater pH adjustment, and condensate treatment. Sometimes it is economical to feed a high basicity amine of low volatility to the feedwater, and inject a high neutralizing capacity amine into the steam with a satellite feed point. The drawbacks are more product inventory and more feed equipment to monitor and maintain. Table 3-18 shows neutralizing capacities and distribution ratios for common volatile amines.

**Table 3-18**
**Neutralizing Amine Properties**

| **Amine** | **MW** | **neutralizing capacity** | **$K_b$** | **Distribution Ratio (vs pressure psig)** | | |
|---|---|---|---|---|---|---|
| | | **ppm $CO_2$/mg/L amine** | | **0** | **200** | **1000** |
| Ammonia | 35 | 2.59 | $1.8 \times 10^{-6}$ | 10 | 7.14 | 3.57 |
| Cyclohexylamine | 99 | 0.444 | $440 \times 10^{-6}$ | 4 | 23.3 | 9.3 |
| DEAE | 117 | 0.376 | $66 \times 10^{-6}$ | 1.7 | 4.5 | 3.4 |
| MOPA | 89 | 0.494 | $102 \times 10^{-6}$ | 1 | 2.4 | 2.5 |
| Morpholine | 87 | 0.506 | $3.1 \times 10^{-6}$ | 6.4 | 1.6 | 0.98 |
| DEA | 105 | 0.419 | $7.9 \times 10^{-6}$ | 0.004 | 0.11 | 0.07 |
| MEA | 61 | 0.720 | $32 \times 10^{-6}$ | 0.07 | 0.15 | 0.29 |

DEAE = diethylaminoethanol
MOPA = methoxypropylamine
DEA = diethanolamine
MEA = monoethanolamine

The distribution of the amine in the steam is straightforward. The distribution ratio expresses the ratio of the concentration of the amine in each phase, as shown in equation (3-54).

$$\text{DR} = [\text{amine in steam}] / [\text{amine in the boiler}] \qquad (3\text{-}54)$$

However, the concentration itself is not directly evident. From mass balance the entire amine is present either in the steam or in the boiler water. But the relative boiler blowdown and steam flow will affect the absolute concentration of the amine in each phase.

The amine in each phase is calculated from:

$$\text{mg/L in steam} = \text{mg/L in FW} \times \text{DR} / (\text{DR} \times \text{S/FW} + \text{BD/FW}) \qquad (3\text{-}55)$$

$$\text{mg/L in BD} = \text{mg/L in FW} \times 1/(\text{DR} \times \text{S/FW} + \text{BD/FW}) \qquad (3\text{-}56)$$

Where FW, BD, S, and DR are the feedwater flow, blowdown flow, steam flow and distribution ratio respectively.

Note that the sum of equation (3-55) times steam flow and equation (3-56) times blowdown flow is equal to the amount of amine in the feedwater, as it must for mass balance to be maintained.

In complex steam distribution systems with flash tanks, the application of neutralizing amines is very complicated. Amines will condense in the flash tanks, and redistribute according to the local relative flow rates and pressures. The proper pH in the flash tank blowdown is important for corrosion protection. Also, the persistence of amine in the steam phase downstream of the flash tanks must be considered.

It is common practice to blend amines for feedwater pH control. One amine is chosen for its ability to raise the pH of the feedwater (more basic amines), while another may be chosen for its neutralizing capacity and/or distribution into the steam.

Low DR amines will concentrate in the condensate, providing good tank protection, but are removed according to equation (3-51). Many satellite feeds may be needed. A high DR amine will remain in the steam, and not provide as good protection to the tank, but will travel further down the system, and provide better protection at distant locations. An amine with high basicity or neutralizing capacity might help overcome this problem, since it will produce a higher pH in the condensate at lower concentration.

### 7.7.4 Filming Amines

Filming amines are used for condensate systems only. Filming amines are high molecular weight amines with long hydrocarbon chains. Most are insoluble in water. The nitrogen end of the molecule is highly polar, and adheres to metallic oxides on the condensate line walls. The hydrocarbon chain is very hydrophobic, and provides protection for the metal surface by preventing contact with water.

The main filming amine is octadecylamine (ODA), $CH_3(CH_2)_{17}NH_2$. It is a very waxy material at room temperature, and must be heated in order to be fed. Feed is accomplished by heating the amine so that it flows freely, then mixing it in with demineralized water. It is then fed directly into the steam header with an injection quill. Stainless steel or Hastelloy is needed, as the concentrated solution is aggressive to steel or copper alloy metallurgy. ODA is sometimes fed as the acetate salt, which is more soluble. The acetate decomposes to liberate ODA and a small amount of acetic acid.

The feed rate is based on steam flow, and is typically about 1 to 5 mg/L active amine. The solution should be held at elevated temperature, around 100 °F. Make down water should be demineralized water or condensate. Solutions fed directly to steam should be free of dissolved solids. Also, since dissolved solids can coagulate filming amines, they should not be fed to systems with high carryover from the boiler.

The feed need not be continuous unless fed to high flow velocity areas. The films are persistent, and may need to be maintained only by intermittent feed. Once a day for a few hours may be enough to maintain good protection.

Use of filming amines in complex steam distribution systems is a problem. Many satellite feed points are needed, as the amine does not travel as far in the steam as the more volatile neutralizing amines.

Filming amines can undercut old oxide deposits and cause them to slough off. The deposits then travel at high velocity in the steam line, leading to erosive wear or clogging of steam traps and valves. For that reason, use of filming amines in older systems should be carefully considered before a decision is made to feed them.

### 7.7.5 Volatile Oxygen Scavengers

All the scavengers discussed in section 7.2 in this chapter, except for sulfite and ascorbate, are volatile. They will pass over into the steam and provide metals passivation in the condensate system. As was noted in that section, the scavengers have the ability to reduce unprotective oxides to the passive magnetite and cuprite forms. Sometimes volatile oxygen scavengers are fed to the steam directly for passivation of the condensate system. Because parts of the condensate system may be under vacuum, air inleakage is always a problem.

The combination of filming/neutralizing amines with a metals passivator (oxygen scavenger) can be a very potent approach to condensate system protection.

In all cases, the selection of any material for direct injection must take into account the possible health and safety effects of these products. Steam is used for air heating and humidification, and direct and indirect contact with food or food packaging materials

## 7.8 CHEMICAL FEEDPOINTS

Boiler chemicals are fed to the feedwater, deaerator, boiler, and steam, depending on their intended use.

### 7.8.1 Internal Treatments

Internal boiler water treatments include various phosphates, phosphonates, polymers, chelants, caustic, nitrite, molybdate and nitrate. They can be fed to the feedwater based on boiler cycles, or to the boiler. If attemperator water is taken from the feedwater, injection of any non-volatile components should be done after the attemperator takeoff.

If orthophosphate is used as an internal treatment, it should never be added to the feedwater line, to avoid possible plugging with calcium phosphate.

If chemicals are fed to the boiler, the feed rate is based on boiler blowdown. In some cases, where blowdown is very intermittent, feed is done in slugs. The chemicals enter the boiler in the drum. Good design will preclude close proximity of the feed line with drum internals. Often the concentrated forms of these chemicals can be aggressive to steel.

### 7.8.2 Oxygen Scavengers

Oxygen scavengers are fed to the deaerator downcomer or storage tank. The feed rate is based on oxygen residuals. Feed upstream of the deaerator is uneconomical because of the mechanical action of the deaerator. Always feed downstream of the deaerating section of the deaerator.

In steam systems, oxygen scavengers can be fed to the main steam header or satellite points as needed.

With hydrazine or carbohydrazide, avoid the use of stainless steel or molybdenum containing alloys.

### 7.8.3 Condensate Treatments

Condensate treatments are fed to the feedwater after the deaerator and after any polishers. This will avoid uneconomical removal of some of the chemical in these units. Direct injection into the steam header is also used. An exception is feed of filming amines; these must be fed directly to the steam header.

Satellite feed points are used to allow condensate treatments to reach distant parts of a complex steam distribution system, or to provide targeted treatment to parts of the system that require special treatment.

Most satellite feed systems involve direct injection into steam lines. They are used to feed filming amines, metal passivators, and neutralizing amines. Usually an injection quill is used. The quill is inserted about halfway into the line, and oriented to feed in the downstream direction.

Filming amines do not distribute well in the steam, and so must be fed at points relatively near where their actions is needed. High velocities degrade amine films, and so they must be fed continuously in these areas. In lower flow areas intermittent feed can be effective.

## 7.9 FEEDING AND CONTROL EQUIPMENT

There is a variety of OEM equipment available for feeding, controlling and monitoring boiler chemical treatments and boiler systems in general.

### 7.9.1 Pumps and Feed Tanks

Feed pumps are positive displacement types to eliminate slippage at high discharge pressures. The pumps must be able to pump against the pressure, which can range from 15 psi to over 2000 psi, depending on the boiler. Typical pump rates are a few tenths of a gallon per day. Most pumps are controllable with a 4-20mA current loop control system. Some pumps are strokable with an external signal generator. Drawdown glasses are often used in these feed systems.

The typical feed arrangement is to use a day tank. This is a cylindrical tank with a condensate feed line for dilution water, a mixer, a sight glass, a cover, and a drain to the pump intake. Enough chemical is added to last for one to a few days' operation. Dilution water is added to dilute the chemical to the appropriate concentration for feed with the existing pump, based on target feed rates.

Example: an amine is to be fed to the feedwater at 3 mg/L active. The amine is a 90% active material with a specific gravity of 1.05. The feedwater rate is 12,000 pph. A three day supply of chemical is desired. The pump is controllable to 0 to 0.5 gph. The tank is 32 inches in diameter. How much amine is needed? How much water is added? What pump speed is used?
First determine the amount of amine needed:
12,000# FW / hr x 3 x$10^{-6}$ # amine/# FW x 72 hr = 2.592 # amine
Next determine the concentration needed in the day tank at maximum pump speed:
2.592#/72 hr x 1 hr/0.5 gal = 0.072 #/gallon
Next determine the gallons of chemical feed needed:
2.592 # amine / 0.072 # / gallon = 36 gallons
Next determine the depth of water in the tank:
36 gal x 144 $in^2$ /$ft^2$ x 12 in/ft / ( 7.48 gal /$ft^3$ x $\pi$ x $16^2$ $in^2$ ) = 10.35 in
Finally, determine the volume of amine to be added:
2.592 # amine x 1# product / 0.9 # amine x 1 gal product / (8.34 x 1.05) # = 0.33 gallons = 1245 cc
Now, it isn't good practice to operate at the extreme limit of the equipment. So, instead, pick a pump speed of 0.35 gph (70% of the maximum). Now, the amount of amine stays constant. The # / gallon must increase to compensate for the lower pump speed. The total #/gallon will now be 0.072 x .5/.35 = 0.103 #/gal. The total volume now decreases to 36 x .35/.5 = 25.2 gallons. This will require a depth of 10.35 x .35 /.5 = 7.25 in.

Finally, use a 15 to 25 % excess of product in the tank to prevent run out of product. The amount of amine increases by 15 to 25%, the gallons in the day tank increase similarly, and the depth also increases by the same factor.

## 7.9.2 Controls

Controls are rapidly changing. Many OEM systems are available. Tank level sensors, pump controllers and flow sensors can be used to control feed rates. On-line analyzers for dissolved oxygen, oxygen scavenger, phosphate, iron, sodium, silica, and pH and conductivity are available. All require sample cooling.

Control schemes can utilize either feed back or feed forward mode:.

Feed back: A feed back controller uses a signal proportional to the quantity to be controlled, e.g. phosphate. If the signal is below the desired level, then feed is initiated at a constant rate. When the signal reaches the desired level the feed stops. The concentration of the desired species oscillates about the desired level. The oscillation is dependent on the dead band of the equipment and the size of the system and equipment. Typically, the oscillations are larger than for feed forward systems.

Feed forward: A feed forward control scheme uses a signal from a control parameter other than the desired parameter itself. For example, to control phosphate a flow signal or pH signal can be used. The feed of product is proportioned to the signal by an appropriate algorithm. Additionally, a secondary signal can be used as a trim control. For example, flow can be the primary signal, and pH can be a trim. The feed rate is proportioned to the flow and is adjusted based on pH. That is, the feed rate changes with flow to maintain a constant feed concentration, but the concentration is changed based on system chemistry changes. Feed forward systems anticipate variances in system performance and adjust accordingly. They tend to lead system changes. Characteristically, they have smaller control fluctuations. Feed forward controllers are more complex and expensive than feed back controllers, but they can provide more precise and uniform control within a smaller band.

## 7.10 CHEMICAL TREATMENT IN LOW AND MEDIUM PRESSURE BOILERS

For convenience, this section summarizes the chemical treatment programs commonly used in low and medium pressure firetube and watertube boilers. For details of these programs, refer to the previous paragraphs in section 7.0 of this manual.

## Table 3-19
## Low and Medium Pressure Boiler Water Treatment Programs

| Chemical | Purpose | Comments |
|---|---|---|
| Sodium hydroxide<br>NaOH - caustic soda | Increase alkalinity, raise pH, precipitate magnesium | Does not form $CO_2$ giving better pH control in steam |
| Sodium carbonate<br>$Na_2CO_3$ - soda ash | Increase alkalinity and pH precipitate calcium | Carbonate breaks down to form $CO_2$ in steam |
| Sodium phosphate<br>$NaH_2PO_4$, $Na_2HPO_4$<br>$Na_3PO_4$, $(NaPO_3)_x$ | Precipitate calcium as hydroxyapatite | Alkalinity and resulting pH must be kept high enough for this reaction. Phosphates may be either acid or alkaline |
| Chelants<br>EDTA, NTA | Control scaling by forming heat stable soluble complexes with calcium and magnesium | Prevents precipitation of scale forming compounds. Must use oxygen free and softened water. Overfeed will cause corrosion |
| Polymers,<br>Polyacrylate,<br>Polymaleates,<br>AA/AMPS | Disperse sludge and distorts crystal structure of calcium deposits to prevent scaling, prevent fouling due to corrosion products | Crystal distortion prevents precipitation from adhering to heat transfer surfaces |
| Tannins, starch<br>Lignin derivatives | Prevents feedwater deposits, coats scale crystals to prevent scale from adhering to heat transfer services | Organic dispersant used with carbonate and phosphate programs. Also distorts scale growth, inhibits caustic embrittlement |
| Sodium sulfite<br>Sodium metabisulfite | Prevents oxygen corrosion in the boiler | Neutralizes oxygen by forming sodium sulfite. Catalyzed forms are much faster acting |
| Filming amines<br>Octadecylamine, etc | Controls condensate corrosion by forming a protective film on metal | Protects against oxygen and acid attack. Relatively difficult to feed and control |
| Neutralizing amines<br>Morpholine<br>Cyclohexylamine<br>Diethylaminoethanol, | Controls condensate corrosion by raising pH | Protects by neutralizing any carbonic acid formed due to the presence of carbon dioxide present in the steam or absorbed in vented condensate receivers |
| Antifoams<br>Polyglycols,<br>Silicones,<br>Polyamides,<br>Propylene oxide | Reduces the foaming tendencies of boiler water | Usually added with other chemicals for scale control and sludge dispersion |

## 8.0 Performance Testing and Monitoring

### 8.1 OVERVIEW

Boiler performance involves pressure, flows, steam quality, and steam purity. Pressure is monitored by pressure gauges and is expressed as psia or psig (pounds per square inch absolute or gauge). Absolute pressure is the pressure measured from zero pressure, or a vacuum. The gauge pressure is the differential pressure between the steam pressure and the ambient pressure (usually taken to be one atmosphere, or 14.7 psi). To convert from absolute to gauge pressure subtract 14.7 psi, and to convert from gauge pressure to absolute add 14.7 psi.

Other pressure measures are bar and Pascal (Pa). Table 3-20 shows the relationship of various pressure measures. Table 3-21 provides conversion factors among various pressure measures.

**Table 3-20**

**Pressure units**

| ATM | BAR | Pa |
|---|---|---|
| 1.013 BAR | .9870 ATM | 9.8X10$^{-6}$ ATM |
| 101325 Pa | 100,000 Pa | 10$^{-5}$ BAR |
| 14.7 PSI | 14.503 PSI | 1.45X10$^{-4}$PS1 |

**Table 3-21**
**Pressure Conversions**

| Psi | Atmos. | Ft head H2O | in H20 | Kg/cm^2 | Meters | In Hg | mm. Hg. | cm. Hg. | bar | Millibar | KPa |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | at 20°C | | | H20 | at 20C | | | | (mbar) | |
| 1 | 0.07 | 2.31 | 27.72 | 0.07 | 0.70 | 2.04 | 51.88 | 5.19 | 0.07 | 68.95 | 6.90 |
| 14.70 | 1 | 33,659 | 407.51 | 1.03 | 10.35 | 30.02 | 762.48 | 76.25 | 1.01 | 1013.00 | 101.33 |
| 0.43 | 0.03 | I | 12.00 | 0.03 | 0.31 | 0.88 | 22.45 | 2.25 | 0.03 | 29.84 | 2.96 |
| 0.04 | 0.00 | 0.83 | 1 | 0.00 | 0.03 | 0.07 | 1.87 | 0.19 | 25 | 2.49 | 0.25 |
| 14.23 | 0.968 | 32.87 | 394.41 | I | 10.02 | 29.05 | 737.96 | 73.80 | 0.981 | 98O.662 | 98.066 |
| 1.42 | 0.10 | 3.29 | 39,370 | 0.10 | I | 2.91 | 73.80 | 7.38 | 0.10 | 98.066 | 9.81 |
| 0.48 | 0.03 | 1.13 | 13.58 | 0.03 | 0.35 | 1 | 25.40 | 2.54 | 0.03 | 33.75 | 3.38 |
| 0.02 | 0.00 | 0.05 | 0.53 | 0.00 | 0.01 | 39 | 1 | 0.10 | 0.00 | 1.33 | 0.13 |
| 0.19 | 0.01 | 0.45 | 5.34 | 0.01 | 0.14 | 0.39 | 10.00 | 1 | 0.01 | 13.29 | 1.33 |
| 14.50 | 0.97 | 33,514 | 402.16 | 1.02 | 10.21 | 29625 | 752.47 | 75.25 | 1 | 1000.00 | 100.00 |
| 0.01 | 0.009 | 0.03 | 402 | 0.00 | 0.01 | 0.03 | 0.75 | 0.08 | 0.00 | 1 | 0.10 |
| 0.15 | 0.01 | 0.34 | 4.02 | 0.01 | 0.10 | 0.30 | 7.53 | 0.75 | 0.01 | 10.00 | 1 |

Flows are important measures because they allow for the calculation of chemical feed rates and blowdown schedules. They also are a measure of the boiler efficiency. The energy provided by the boiler is a product of the flow rate and the operating pressure. Flows are measured by flow meters, which show both the instantaneous flow rate and the cumulative flow. The boiler operator should routinely log both measurements.

Chemical levels are of critical concern for several reasons:

- They indicate if the proper level of chemical is present
- They provide a measure of how much needs to be added
- They provide data on treatment costs
- They can indicate if there is a problem with boiler control or internal problems such as deposition or corrosion
- They can indicate if the steam separation equipment or deaeration equipment is operating properly

Chemical levels are determined by taking a cooled sample of the flow under study (feedwater, boiler water, condensate, or steam). The sample is then analyzed by wet chemistry, instrumental means, or visual comparison (such as filter pads). Appropriate chemical levels for the various programs are discussed in section 7.0

System protection is also an important monitoring objective. Besides measuring chemical levels and operating factors such as dissolved oxygen and conductivity, the measurement of corrosion products in the feedwater can indicate if there will be a corrosion problem in the boiler. For example, excessive copper in the feedwater can lead to tube blockage in the boiler. The tube blockage can lead to rapid overheat failure.

Corrosion products and other impurities in the boiler water can also be carried over into the steam in significant amounts. This can pose a problem for downstream equipment and processes, where those impurities can deposit. Turbines are especially vulnerable to high levels of silica, copper and caustic in the steam. Even in low and medium pressure systems, boiler carryover can lead to problems in process equipment and to corrosion and deposition in condensate lines.

Corrosion coupons can be used in boiler systems. For obvious reasons, the handling of these items is significantly more complicated than for cooling system corrosion coupon measurements. In addition, metal samples for caustic embrittlement and stress cracking have been used.

## 8.2 SAMPLING

The purpose of sampling is to determine if the chemical and water parameters are correct, or to detect problems in corrosion control or deposition control. In any sampling program, one must take into account the available sample points, the criticality of a particular measurement and the available means for analysis. A sampling schedule should be developed. Some parameters should be logged on a frequent basis, while others need only be logged infrequently.

### 8.2.1 Sample Cooling

Procedures for obtaining water and steam samples for analysis in a boiler system are also more complicated than in a cooling water system. ASTM specification D1066-82 deals with steam sampling standard practice. ASME specification PTC 4.1, part 11 deals with sampling of water and steam.

All samples must first be conditioned by cooling to an appropriate temperature. Condensate is typically available at temperatures of about 100 to 120 deg. F., so that little if any further cooling is needed. For hot water and steam samples, a simple temporary cooler can be made from a throttling or needle valve, stainless steel tubing and a bucket of cold water. However, for permanent installation, or where precise control of the sample temperature is required, more sophisticated coolers are required.

A sample cooler consists of tubing (typically ¼" stainless tubing with Swagelok® fittings), a precooler and sometimes a fine cooler. A gate valve can be used for the main flow, and needle valves for fine flow control. Typical sampling flow rates are 20 to 100 ml/min. Optionally, a filter can be employed after the rough cooler.

Where temperature control is important, sizing of the coolers is complex. In general, one takes the enthalpy of the sample stream (from steam tables), and the enthalpy of the final cooled sample. The difference is multiplied by the flow rate in appropriate units to get the total BTU per unit time to be removed. Then the temperature of the available cooling water is obtained, and the difference between that and the final desired sample temperature is determined. A factor of 1 BTU/lb-deg is acceptable for sizing purposes. The flow rate of the cooling water is then determined. A factor of 70% for the efficiency of the cooler is adequate, and a residence time of at least ten seconds is needed. If rough and final coolers are used, the rough cooler should cool the sample to about 15 to 25 deg. F above the desired sample temperature. Figure 3-21 shows a typical sample cooler.

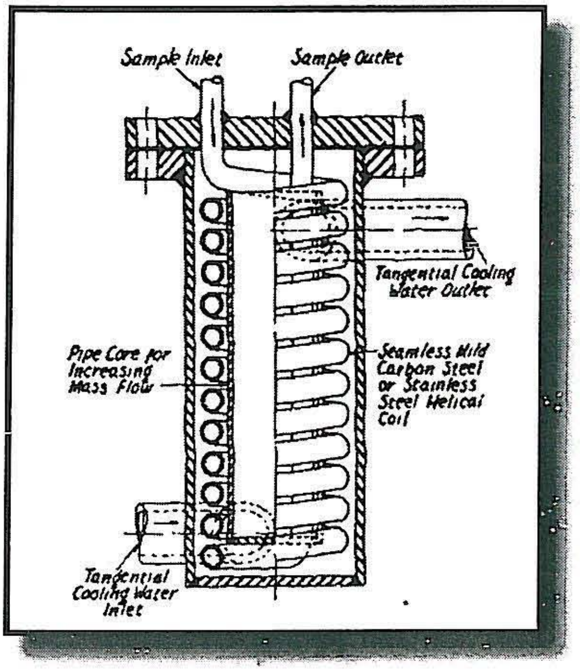


**Figure 3-21. Sample cooler**

If water samples are required for instrumentation, the manufacturer's manual should be consulted for the proper temperature range. Continuous

**Example: a 600 psig steam line is to be cooled for sampling to 75 deg. F. The cooling water is at a temperature of 55 deg. F. Assume 100 cm$^3$ /min maximum sample flow, and 70% efficiency for the cooler. What is the coolant flow needed, and how long should the cooler tube be for a 10 second residence time?**

**From Steam Tables, H$_{600\ psi}$ = 1203.7 BTU/lb, H$_{75\ degF}$ = 43.04 BTU/lb.**

**The heat to be removed is 1203.7 – 43.04 = 1160.66 BTU/lb.**

**At 100 cm$^3$ /min flow rate the total heat removed per minute is**

**100 cm$^3$ /min x 1 g/cm$^3$ x 1 lb / 454 g x 1160.66 BTU/lb = 255 BTU/min**

**The final temperature difference between the cooling water and the sample is about 5 degrees F, so the final coolant temperature will be about 70 deg. F. The flow rate of water needed is given by**

255 BTU/min x 1#-deg/BTU x 1/(70 – 55) deg F. x 1 gal/8.34 lb x 1/.7 (efficiency) = 2.9 gpm

**The length of the cooling path is given by**

**100 cm$^3$/min x 1/($\pi$ (0.25/2 in)$^2$ x (1 in/2.54 cm)$^2$ x 1 min/60 sec x 10 sec = 53 cm = 20 in**

analyzers for silica and sodium require near-ambient temperatures. Instruments for on-line pH and dissolved oxygen monitoring also require near-ambient temperatures to protect the membranes and housings. Conductivity cells can tolerate significantly higher temperatures.

### 8.2.2 On-Line Sampling

On-line analyzers include pH, conductivity, silica, sodium, phosphate, dissolved oxygen and cation conductivity. High pressure, field-erected boilers will include many or all of these analyzers. For smaller boilers such as package boilers for process or turbine power, only the lower end analyzers will generally be used. These include pH and conductivity. Generally, the other parameters are determined by grab sample analysis. Of course, cation conductivity must also be an on-line measurement, as air intrusion will render the results meaningless.

For corrosion product analysis, the flow rate must be at least 70 $cm^3$/min in order to prevent metals hideout in the sample line. For very precise work, a nitric acid injection system must be used. Nitric acid is injected as a 1-5% solution, and at a rate to produce a pH of 2 or less in the sample stream. The acid must be injected before the coolers to prevent metal hideout in the coolers. For this purpose a stainless steel positive displacement pump should be used to prevent pump corrosion, and to pump against the sample line pressure. If nitric acid injection is used, the sample line should flow for at least 10 minutes before a sample for analysis is obtained.

## 8.3 TESTING

Testing is used to control the treatment program and boiler water quality. Testing is done by on-line instruments and by grab sample analyses. The frequency of the analytical testing is determined by the criticality of the process and the safety factor for the boiler. Low-pressure units are more forgiving, and can be controlled with fewer analyses and longer periods between samples. In general a boiler should be monitored daily. Higher-pressure units should be monitored once per shift. High pressure, field-erected boilers need continuous on-line monitoring for most parameters.

### 8.3.1 Purpose of Analyses

- pH: Measures various factors.
  - Feedwater pH is important for corrosion in the feedwater train.
  - Boiler water pH is a measure of chemical program effectiveness.
  - In coordinated phosphate programs, pH is a measure of the control point along with phosphate measurement.

  - In precipitation programs, pH a measure of the ability to precipitate calcium phosphate and magnesium hydroxide, and to solubilize silica.
  - Condensate pH measures neutralization of alkalinity.

  The pH of a cooled water sample is different from the pH at temperature in the boiler circuit (see chapter 1). This can provide misleading results. For example, ammonia becomes increasingly acidic at higher temperatures, and approaches the acid-base behavior of water at very high pressures. A cooled sample may indicate a basic pH when treated with ammonia, but the pH in the boiler may be closer to neutral.
- Hardness: to control the addition of phosphate, chelant, and dispersant, and as a measure of feed water quality.
- Dissolved oxygen: to monitor deaerator effectiveness and control oxygen scavenger feed rates.
- Conductivity: in the feedwater and boiler, to monitor cycles of concentration and prevent exceeding boiler guidelines for TDS.
- Cation conductivity: in the condensate, to monitor for cooling water leaks, in the steam to monitor steam purity.
- Alkalinity: to calculate 2P-M (hydroxide alkalinity, chapter 1) for boiler water precipitation program control (section 7.3 in this chapter).

### 8.3.2 Metals

Metals are a sign of corrosion in the feedwater train, and will deposit in the boiler to create hot spots and corrosion sites. Typically iron and copper are the main species. Monitoring is via wet chemical analysis or by filter pad comparisons. Typical levels are a few ppb to a few hundred ppb. In general, metals can be high during startup, but should drop to low ppb values during base operation. Anything above about 10-15 ppb is indicative of a problem. Suspect oxygen inleakage, poor oxygen control, or poor pH control in the feedwater.

- Iron can be in the ferrous or ferric state; there are specific chemical tests for each. In addition, the iron can be soluble or insoluble. The determination is by analyzing a filtered (0.45 micron or finer) sample and an unfiltered sample. Air contact with the sample should be minimized or the determination of the two iron states will be questionable. The ferrous ion will oxidize to the ferric state on standing, but acidification of the sample will slow the oxidation. Soluble iron will be removed easily by blowdown, but particulate iron will deposit on boiler wall tubes or settle in the lower (mud) drum.

- Copper is generated by corrosion of the feedwater heater tubes or the condenser tubes. It is a sign of excessive oxygen in the feedwater. A significant amount of copper can come from the spalling of copper oxides due to thermal shocking on startup, but a well-operated system should not exceed a few ppb of copper.

Like iron, copper comes in a low (cuprous) and a high (cupric) oxidation state. The copper can also be soluble or insoluble. Soluble copper can galvanically deposit on boiler tubes, leading to hot spot development, galvanic attack, cracking and pitting. Oxides of copper are volatile in high-pressure boilers, with cupric oxide being the more volatile species. Above 20 ppb in the steam, copper can pose a threat to turbine performance. There is no readily available test to distinguish the two oxidation states of copper.

### 8.3.3 Chemical Treatment

Boiler treatment chemicals include nitrite, phosphate, molybdate, chelant, neutralizing amines, and oxygen scavengers. All of these can be analyzed by chemical and/or instrumental means. Also used are polymers of various types, but mostly polyacrylic acid mono- or co-polymers, polymethacrylic acid, polymaleic anhydride co-polymers, and antifoam agents.

Samples are obtained from the sample coolers and tested as indicated. Cooling the sample does not affect the concentration. This is different from the effect of temperature on the pH measurement.

### 8.3.4 Conductivity

Samples should be monitored with an in-line probe. Exposure of the sample to air results in increased conductivity due to carbon dioxide uptake. The most typical conductivity points are feedwater and boiler water. Steam (condensate) conductivity can be an important indicator of poor steam purity caused by poor steam-water separation, poor drum level control, foaming (priming) in the drum, and excessive impurities in the boiler volatilizing into the steam.

### 8.3.5 Summary of Methods

Table 3-22 summarizes ASTM and Standard Methods test procedures for common boiler water parameters.

Table 3-22. Summary of ASTM and Standard Methods Test Procedures

| Test Name | ASTM Number | Standard Methods |
|---|---|---|
| Iron | D-1068 | 3110/3120 3500FeD |
| Copper | D-1688 | 3110/3120 3500 Cu |
| Total hardness | D-1126 | 2340 |
| Calcium hardness | D-1126 | 2340 C/3500 CaD |
| PH | D-1293 | 4500 $H^+$ |
| Alkalinity | D-1067-92 | 2320 |
| Orthophosphate | D-515-88 | 4500-P |
| Sulfite | D-1339 | 4500 $SO_3^{-2}$ |
| Hydrazine | D-1385 | N/D |
| Silica (soluble) | D-859-94 | 4500-Si |
| Sodium | D-2791-93 | N/D |
| Dissolved oxygen | D-888 | 4500-O |
| Conductivity | D-1125-91 | 2520 |
| Oils | D-3291-85 | 5520 |
| Total organic carbon | D-4779-93 | 5310 |
| TDS | N/A | 2540 C |
| Suspended solids | D-3977 | 2540 D |

## 8.4 STEAM PURITY AND QUALITY

### 8.4.1 Steam Purity

This is a measure of the concentration of substances other than water in the steam. Some chemicals are desirable to have in the steam. These include neutralizing amines and oxygen scavengers. But most impurities are undesirable, including silica, copper, sodium, and particulate metal oxides. The latter are usually produced by exfoliation from superheater tubes and main steam headers. Steam purity comprises both volatile substances and dissolved substances carried over by water droplets entrained in the steam.

Specific requirements for steam purity are based on end use of the steam. This is discussed further in section 11.

Volatile metals, sodium and silica will deposit on cooler surfaces like turbine blades. The deposits plug steam pathways in the turbines, lowering efficiency. They can also lead to blade cracking and resulting turbine imbalance. These substances should be held to a minimum (see section 11.0 for limits).

Steam samples are obtained by multiport or isokinetic samplers. These are designed to collect a representative sample of the steam, including the water droplets. Because water and steam will not be evenly distributed across the diameter of the steam header, a specially designed collection device must be used.

The steam sample is cooled and analyzed by conductivity and chemical methods. Also, cation conductivity measurements can be used to measure free mineral acidity in the steam, primarily chlorides and sulfates. To do this, a degassed sample, for removal of carbon dioxide, must be analyzed.

### 8.4.2 Steam Quality

Steam quality is the percent by weight of dry steam in a mixture of saturated steam and suspended or entrained water droplets at the same temperature. Steam quality is important because it is a measure of how efficient the steam separation equipment is, or if there is a problem with drum level control or foaming, the prime causes of carryover. Steam purity is not a reliable measure of steam quality.

Measurements must be made before the superheater, because the steam quality will be changed by the input of heat after the boiler.

Steam quality is measured by a steam calorimeter. This is a device for obtaining a representative steam sample, and then expanding it without the input or loss of heat. The theory is that by expanding the steam sample to a point where the steam is superheated with no input or loss of heat then a temperature change will occur resulting from the vaporization of the liquid fraction.

Steam quality is calculated from the following equation:

$$\% \text{ steam quality} = 100 \times (h_2 - h_f) / h_{fg} \qquad (3\text{-}57)$$

where $h_2$ is the enthalpy of the superheated steam at the calorimeter temperature and pressure (from steam tables).

$h_f$ is the enthalpy of the saturated liquid in the mixture before throttling.

$h_{fg}$ is the enthalpy of vaporization at the pressure of the saturated steam entering the calorimeter.

### 8.4.3 Steam Traps

Steam traps are found on most steam handling systems. Steam gives up some of its enthalpy due to imperfect insulation in the steam piping. As it does so, some of the steam will condense to liquid water. Even superheated steam lines will produce condensation due to length of the line and changes in steam flow. The condensate is often valuable for return to the boiler, and at the same time, condensation points can be sites for localized corrosion in the steam line. A steam trap serves three main functions:

- Serves as a point to return the condensate to a collection system.
- Permits the release of non-condensable gases and air from the steam line.
- Prevents the loss of steam from the system.

There are many designs for steam traps. The most common one is the fixed orifice trap. This is easily recognizable as an inverted "y" in the steam line. It is based on the principle that the flow rate of water through an orifice is much higher than the flow rate of steam. The steam trap has to be periodically opened to permit the flow of condensate to the collection point.

## 9.0 Troubleshooting Boiler Systems

Like all equipment, a boiler and its associated equipment are subject to deterioration and failure. Inspections should be routine. At each boiler outage, the unit should be inspected visually and by destructive analysis. Examples are drum inspections, boroscopic examinations, eddy current testing, and tube removal for metallographic examination and deposit analysis.

### 9.1 BOILER INSPECTIONS

### 9.1.1 General Inspections

- Steam drum: The boiler must be cooled, drained and cleared for confined space entry. The drum is examined first. Look for deposits, broken or corroded internals (feed lines, blowdown lines, steam separators, baffles, etc.). Examine the waterline for pits or tubercles indicating oxygen attack. If shiny metal is visible beneath the tubercle, and if the tubercle has a watery interior, this is indicative of active corrosion. Look for signs of rust. The tubercle interior should be a uniform black-gray, crystalline deposit. The deposit should be magnetic, indicative of magnetite. Inspect the riser tube entry points to the steam drum for signs of damage indicating steam blanketing.
- Mud drum: Check the mud drum for excessive sludge deposits. This is especially a problem if the sludge level is near the riser tube entry points. Blocked riser tubes can fail due to rapid or long term overheat.
- Economizer: Check for signs of corrosion and sludge deposits. Economizers are usually subject to corrosion, especially if oxygen control is poor.
- Deaerator: Deaerators are subject to corrosion and stress cracking. The most vulnerable points are the trays and tray supports. Looks for signs of rusting or cracking. Inspect the chemical injection point for excessive corrosion or wear.
- Feedwater heaters: Look for general corrosion and stress cracking at U-bends or the tube-to-tubesheet roll. The metallurgy is commonly brass, which is subject to ammonia induced stress corrosion cracking. Ammonia is often present due to breakdown of neutralizing amines and thermal decomposition of hydrazine.
- Condensate return system: Inspect valves, steam traps and pipes. Look for excessive accumulation of solids in the strainers and for red water exiting at the drains. Check for oxygen pitting and acid corrosion in the lines. Condensate storage tanks should be inspected for corrosion on the walls and at the crevice in the base of the tank (good tank design should be a conical bottom with no crevices).

### 9.1.2 Corrosion Problems

Corrosion in boiler systems is almost exclusively due to excessive levels of dissolved oxygen. Feedwater lines are prime locations for oxygen corrosion because makeup water is a source of high oxygen levels. Condensate lines are subject to both oxygen pitting and carbonic acid corrosion.

- The deaerator is a prime location for oxygen corrosion, especially in the trays and tray supports. One of the most common problems in tray-type deaerators is collapse of the tray stack. This will greatly diminish the effectiveness of the unit.
- In high-pressure boilers with economizers, the economizer may be the most sensitive part of the preboiler system to oxygen corrosion. The tubes are thinner in this section than in the boiler as a whole, the tune metal is hot, and in a poorly run system, dissolved oxygen levels may be high.
- In the steam drum, excess oxygen collects at the water line. Look at this location for excessive oxygen corrosion.
- Boiler tubes are subject to various forms of corrosion:
    - Oxygen pitting is characterized by a "cratered moon" appearance. Deep, symmetrical hemispherical pits are in evidence, with a lot of overlapping pits within pits.
    - Caustic gouging occurs when excess alkalinity concentrates under deposits by factors of several thousands or ten thousands. The pH can easily exceed 14, and iron forms very soluble species at these pH levels (section 7.4 and chapter 1). Chelant corrosion is exemplified by longitudinal streaks with considerable metal wear. The wear is often concentrated on the hot side of the tubes. Magnetite is not present in these areas, and the tube surface is clean and shiny (section 7.3.5).
    - Acid attack in the boiler tubes occurs when acidic impurities enter the boiler, usually from condenser coolant leaks. Cation resin leaking into the feedwater can decompose in the boiler to form organic acids. The appearance is of a magnetite free surface with many widely dispersed pits and gouges. Also, general thinning of the boiler tubes often occurs.
- In condensate lines, carbonic acid can form from alkalinity breakdown in the boiler. If insufficient neutralizing amine is used, the condensate lines will be attacked by the carbonic acid formed by the dissolution of carbon dioxide in the condensate. The attack takes the form of grooving on the bottom of the line, where the condensate flows.
- Superheaters and steam lines are subject to oxygen attack as well. Metal loss occurs by high temperature oxide formation and exfoliation. The exfoliated oxide particles can cause damage downstream, especially at bends, from erosive wear.

### 9.1.3 Deposits

Deposits form due to the transport of corrosion products from the feedwater into the boiler, where they cement to the hottest part of the tubes. Galvanic deposits form when copper ions travel to the boiler and plate out on the steel surfaces. Hardness and silica can deposit in the boiler if not controlled by a precipitating program or chelant program (section 7.3). Softener or demineralizer upsets can lead to unplanned excessive hardness in the feedwater. Silica deposits form if the pH in the boiler is too low.

Deposits can create locations for the concentration of contaminants in the boiler water to dangerous levels. Caustic, acid, or chelant can concentrate to levels, which are very aggressive to steel. Deposits also thermally insulate the tube ID surface, leading to higher tube wall temperatures. Long term overheating can lead to fatigue failures. These are characterized by thick lipped bursts of the tube wall. Metallurgical examination will reveal a significant change of grain structure in the steel. Such a diagnosis is best left to a metallurgist. Often the deposits that created the problem will be removed by the force of the escaping steam after the failure. Absence of deposits is therefore not a reliable means of diagnosis.

When boilers undergo routine maintenance, some boiler tubes should be cut out for analysis. Deposit weight density (DWD) should be measured on the hot and cold side of the tube. Different means for determining DWD are employed, and each gives a different result for the same specimen. The method of determination should be taken into account when assessing the meaning of the results.

For the mechanical scraping technique for measuring DWD, the following are Babcock & Wilcox (B&W) guidelines for maximum acceptable DWD levels on cleaning of boiler tubes:

| | |
|---|---|
| • Below 1000 psig | 20-40 g/sq ft |
| • 1000-2000 psig | 12-20 g/sq. ft. |
| • >2000 psig | 10-12 g/sq. ft. |

## 9.2 CONTAMINATION PROBLEMS

For a given pressure range and end use of the steam, various steam quality criteria can apply. For safe boiler operation certain contaminants must be eliminated to avoid excessive corrosion and/or deposition. For steam purity, besides efficient steam/water separation in the drum, maintaining low levels of volatile impurities in the steam is essential to limiting the impurities in the steam. Bear in mind that impurities in the feedwater will cycle up in the boiler. So, for example, if 0.5 mg/L of silica is in the feedwater, there will be 15 mg/L of silica in the boiler operating at 30 cycles (3% blowdown).

### 9.2.1 Volatility and Carryover of Boiler Dissolved Solids

Perhaps surprisingly, almost all boiler water dissolved solids have some volatility. By far the most common volatile solid is silica (section 7.6.2). For other boiler solids, the effect is significant only in very high-pressure boilers. For example, at 1500 psia, a steam purity requirement of 20 ppb copper will limit boiler water copper to 333 ppb (0.33 ppm) because of the volatility of copper oxide.

Keep in mind that this effect refers only to soluble (dissolved) solids. Physical carryover is a different problem that can produce high levels of boiler solids in steam. This can be a problem in all types of boilers, over the entire boiler pressure range.

There can be many causes for boiler water carryover into steam. For example:

- Mechanical problems, including failure of mist eliminators, flooding of steam separator drums, improper installation (steam drum not level) and others.
- Operating problems, including over-design operation (over-firing), steam drum water level too high, sudden load changes causing surging (an effect similar to water hammer) and too-rapid startup or shutdown.
- Chemical problems, including excess alkalinity in feed water leading to rapid generation of carbon dioxide in the boiler (chapter 2 and Table 13), too high cycles of concentration leading to dissolved solids levels above ASME guidelines (Table 13) and improper use of antifoams.

### 9.2.2 Oil Contamination

Oil contamination can often be a problem in boiler performance and steam purity and quality. Oil causes foaming in the boiler and also breaks down to organic acids, which can carry over into the steam. The acidic components in the boiler can interfere with program control for precipitation programs and for coordinated phosphate treatments.

Antifoam application can mitigate the foaming and carryover effects. The acidic product formation can be addressed by the addition of caustic to the boiler to neutralize the acids and prevent their volatilization into the steam. If oil contamination is an ongoing problem the system should be inspected to find and correct the sources of contamination. Possible sources include pumps and valves, or leakage from demineralizer units. The boiler should be considered for a caustic boil out during an outage to remove residual oil contamination.

### 9.2.3 Chemical Cleaning

Chemical cleaning is complex, and fraught with many dangers and problems. Among them are damage to the boiler, safety concerns, and disposal regulations. For this reason, only companies specializing in this service should perform cleanings. The recommendation to clean is generally based on boiler inspections during outages (section 9.1.1).

Chemical cleanings are usually acid or chelant based. Acid cleaning usually involves hydrochloric acid with inhibitors as a liquid or foam. Citric acid is also used. Chelant cleanings usually use EDTA, and are conducted at basic pH. Copper deposits are removed by copper-specific chelants like thiourea, or by oxidizing cleaners like bromate, peroxide, or persulfate.

New boilers are subjected to alkaline boil-out to remove mill scales and residual oils. After any repairs that might have created oil or grease contamination in the boiler, an alkaline boil-out should be considered. Boil-out chemicals are based on trisodium phosphate. Caustic or soda ash should never be used for this purpose.

### 9.2.4 Metallurgical Failure Analysis

Some of these concepts were discussed in sections 9.1.1 and 9.1.2. Generally, destructive testing is carried out. Boiler tubes are cut out for metallurgical analysis.

- Deposits: Look for watery deposit interiors, which are signs of active corrosion. Shiny copper deposits indicate galvanic attack, and may cause long term overheating.
- Pits and gouges: Examine the morphology. Hemispherical pits with sharp edges are indicative of oxygen attack. Irregular deep gouges are signs of caustic attack, while shallow gouges with the appearance of rivulets are often acid attack. Moisten a piece of universal pH paper and touch it to the damaged area to measure the surface pH. Acid attack can also appear as a rough, grainy, uniform surface.
- Grooved areas which are clean can be chelant attack, while deep general areas of penetration can be steam blanketing. This results from tube overheating and subsequent reaction with the steam.
- Tube failures: Thick lipped bulges with longitudinal cracks or bursts are due to long term overheat or thermal fatigue. The metal becomes plastic and creeps. This is accompanied by changes in the grain structure. Thin lipped bursts with sharp edges result from short term overheat, usually due to water starvation from tube blockages.
- Large irregular shaped windows with no tube thickness alteration are caused by acid attack. The acid forms hydrogen gas, which then reacts with carbon in the steel to form methane gas. The resulting decarburization

weakens the grain structure. A sudden loss of strength results in a blow out of a jagged piece of the tube. Tube thinning is not involved.

## 9.3 OPERATING PROBLEMS IN LOW AND MEDIUM PRESSURE BOILERS

Table 3-23 provides a summary of common operating problems encountered in low and medium pressure boilers. Sections 7.0, 8.0 and 9.0 in this chapter contain information about these problems.

**Table 3-23**
**Operating Problems in Low and Medium Pressure Boilers**

| Pressure | Phenomenon | Causes |
|---|---|---|
| | **Scale Problems** | |
| Low | Hardness and/or silica scale On heating surfaces and drum. | Poor water quality.<br>Poor softener operation.<br>Poor boiler blowdown control.<br>Insufficient chemical treatment. |
| Medium | Mainly iron oxide deposits in High thermal loading sections. | Poor water quality.<br>Fouled ion exchange resins.<br>Clarifier carryover.<br>Corrosion products.<br>Process contamination.<br>Wrong chemical injection point. |
| | **Corrosion Problems** | |
| Low | $O_2$ & $CO_2$ corrosion of heating surfaces, feed & condensate lines.<br>Under-deposit corrosion on Heating surfaces. | Poor pH control.<br>$O_2$ in feedwater.<br>Corrosion products in condensate.<br>Corrosion during layup periods. |
| Medium | Corrosion product scale on Heating surfaces.<br>Caustic corrosion.<br>$O_2$ & $CO_2$ corrosion of heating surfaces, feed & condensate lines. | Corrosion products from feed or condensate lines.<br>Poor pH control.<br>Poor $O_2$ scavenging.<br>Poor pH & P-alkalinity control In boiler.<br>$Na^+$ ion leakage into boiler.<br>Corrosion during layup periods. |
| | **Carryover Problems** | |
| Low | Decreased steam purity.<br>Product quality problems.<br>Corrosion in condensate lines. | Sudden load changes.<br>Poor boiler controls.<br>Conductivity too high..<br>Steam separator or feedwater problem.<br>Process leakage into boiler.<br>$O_2$ and $CO_2$ in boiler. |
| Medium | Scale formation in turbines.<br>Corrosion in condensate lines. | High silica level in boiler water.<br>Suspended solids in feedwater.<br>Poor chemical injection point.<br>Sudden load changes.<br>$O_2$ and $CO_2$ in boiler.<br>Process leakage into boiler. |

## 10.0 Boiler System Operations

This section is intended as an overview only, for general information and understanding. Actual operation of boilers should be handled by certified or licensed boiler operators.

### 10.1 BOILER OPERATIONS

#### 10.1.1 Base Loaded Boilers

Base load boilers are intended for long uninterrupted runs. They operate for 300 days or more between shutdowns for maintenance. They are not subject to much thermal stress, although they may undergo daily load fluctuations. These are the easiest boilers to operate because they do not undergo much thermal stress from repeated heating and cooling cycles.

#### 10.1.2 Peaking Boilers

Peaking boilers are designed to provide additional steam when demand is unusually high. They are designed to undergo numerous thermal cycles, and as such are of heavy-duty construction. They are also simpler to operate, so that they can be brought on line quickly with a minimal crew. They are subject to higher corrosion rates because they are frequently cooled down, making oxygen in-leakage significant. Correspondingly, metal transport into the boiler can be a problem.

#### 10.1.3 Variable Load Boilers

The main problems in variable load boilers involve drum level control. As load suddenly increases, the sudden release of steam lowers the drum pressure, causing an initial increase in drum levels. In this case, a commonly-used feedback drum level controller would compound the problem. The rapid drum level rise would cause a cutoff of drum feed. This can lead to a drying out of the drum. Soon, a rapid demand for feedwater would cause a cooling of the boiler with subsequent drops in drum level.

With load decreases the opposite would occur. An initial drop in drum level occurs as gas bubbles are compressed. The drum controller calls for more water even as steam load is decreasing.

In both cases, a single element controller changes initially in the wrong direction. More complex controller schemes using steam flow and fuel firing rates can be used to provide a more even control mechanism.

Low load operation is difficult to control because the controllers and sensors have poor response profiles at low steam flows. Manual adjustment is frequently needed.

## 10.2 STARTUP, SHUTDOWN AND LAYUP

### 10.2.1 Startup Procedures

Following is a general routine used for starting up a boiler system from a cold shutdown. Site-specific changes must be made as needed.

All valves must be checked and placed in their startup positions. The upper drum vent valve is opened and water filling is started. Other valves may need to be opened as well, such as sight gauge valves and water column shutoff valves. Oxygen scavengers and condensate amine treatments should be added with the fill water. Boiler treatments should be added to the steam drum.

The fuel system is brought on line with the appropriate procedures (purging and venting). Leaving the steam drum vent valve open, the system is fired and brought to about 15 psig to vent noncondensable gases. Then the drum vent valve is closed and firing is continued to bring the boiler to operating pressure.

Water levels are monitored carefully during startup. At various pressures, a hold may be maintained to check for chemistry limits (section 11). Once the guidelines are achieved, the system may be brought to full operating pressure. The main steam throttle valve is then opened and the boiler is placed on line.

### 10.2.2 Shutdown Procedures

Load is gradually reduced and firing is reduced and then shut down. The unit is blown down at a high rate to reduce suspended and dissolved solids. The boiler is brought to feedwater chemistry conditions as closely as possible. The fire side draft fans are run until the unit is cooled.

If the boiler is to be layed-up for any significant period, then lay-up procedures should be followed.

### 10.2.3 Layup Procedures

Layup is designed to permit the boiler to remain at ambient conditions for long periods of time without creating corrosion problems, and also to expedite a rapid return to service. The type of layup depends on the anticipated outage. If the unit is expected to be out of service for months or longer, dry layup should be used. The advantages are a minimization of corrosion. The main disadvantage is the cost and time required to refill and start up. For shorter outages, wet layup is recommended.

For dry layup, as much water as possible is drained, and heat is maintained to dry out the boiler elements. A nitrogen or steam blanket is applied to exclude air. A positive pressure must be maintained to keep air (oxygen) out of the boiler.

For wet layup, the boiler is completely filled with deionized water, pH adjusted with amines or ammonia, and treated with high levels of an oxygen scavenger.

The typical level is from 100 to 500 mg/L of active scavenger such as sulfite or hydrazine. The water should be tested periodically for metals, oxygen scavenger and dissolved oxygen. If metals begin to concentrate in the water, more oxygen scavenger should be added.

Volatile corrosion inhibitors, also called vapor phase corrosion inhibitors, provide a new and very effective way to treat boilers for extended wet layup. These inhibitors are added to the water as the boiler is filled for layup. They exist both in the water and in nay vapor space that develops, and they help to prevent corrosion by any oxygen that may enter the boiler. Manufacturer's instructions should be followed carefully to ensure that the correct inhibitor is selected and properly dosed.

## 10.3 SAFETY IN BOILER OPERATIONS

Water treatment personnel must always remember that a boiler plant and the operating equipment in the plant are hazardous. It is vitally important to know, understand and follow all facility safety regulations. If an accident happens, ignorance of the regulations will never be an acceptable excuse.

Also, never follow an operator around a boiler plant when it is obvious that he/she is not obeying the safety regulations. Operators may become careless with routine work. Follow all regulations, and if necessary, discuss safety issues with the operators and with management.

- Following are some general rules of conduct in any boiler house, regardless of boiler pressure:
- Always wear appropriate safety equipment, including safety glasses and hearing protection. Lost eyesight and hearing cannot be found again.
- In operation, remember that a boiler is hot, and under pressure. Avoid entering the boiler area unless it is necessary. Never underestimate the power of escaping steam, even in very low pressure boilers.
- Valves can leak hot steam or condensate. Be very careful with valves.
- Never attempt to force a valve, and never put a wrench on a pipe under pressure, even if it seems that a simple turn will correct a small leak. If the pipe threads are corroded, the pipe may break off in your hands.
- Do not assume that an uninsulated pipe is not hot.
- When obtaining samples, make sure the cooling water is flowing in the sample cooler before sample valves are opened.
- Boiler chemicals are often hazardous for contact, inhalation or ingestion. Exercise caution in entering chemical storage areas and when handling chemicals. Read all applicable Material Safety Data Sheets.

- Entry into the boiler drum or furnace for inspections should only be done by following confined space entry procedures. Lockout and tag out procedures must also be followed and respected when entering an area.
- Never work alone in an operating boiler room. Always have a partner or an operator with you, even if you are just doing routine testing, and make sure that someone in the control room or the plant office knows you are there. Bad accidents can happen instantaneously, and there may be no time to call for help.

## 11.0 General Guidelines for Boiler Operations

There are several areas of concern for general operations. These include boiler water chemistry and operating guidelines, and Food and Drug Administration (FDA) limitations and guidelines. The American Boiler Manufacturers Association (ABMA) and the American Association of Mechanical Engineers (ASME) have issued consensus guidelines for water quality according to boiler pressure range. Some of the quality guidelines are related to safe boiler operation, and others are related to steam purity requirements for various end uses. A copy of the consensus guidelines can be obtained from the American Society of Mechanical Engineers, 345 East 47th Street, New York, NY 10017.

FDA guidelines are always changing, so that any listing here may be out of date at any time. It is best to consult the Code of Federal Regulations (CFR) for the most current applicable standards and regulations. (Section 21 CFR 173.310).

### 11.1 ABMA/ASME CONSENSUS GUIDELINES

Table 3-13, in section 7.6.1, details the consensus guidelines for feedwater and boiler water for water tube boilers with drums. These are guidelines only, and are based on consensus rather than absolute limitations. Many of these guidelines are related to steam purity, and thus are end-use related, for example turbine quality steam.

### 11.2 FDA GUIDELINES

FDA guidelines apply to boilers producing steam that is intended to contact foods or food packaging materials, or for air heating and humidification. Consult 21 CFR 173.310, and 21 CFR 176.170 or 180 for paper product regulations.

### 11.3 OTHER CHEMICAL TREATMENT LIMITATIONS

Chemical treatment limits and guidelines are discussed in section 7.0. Treatment limitations are related to fouling or corrosion potential, or to effects on steam purity. Chelant levels, alkalinity control, phosphate levels, polymer levels and pressure range limits must all be carefully considered for each boiler system. Two apparently identical boilers may be producing steam for different uses, or may be in different operating modes, and therefore may require entirely different chemical treatment programs.

Oxygen scavenger breakdown to ammonia can cause condensate system problems. Never exceed the established dosage limits for any oxygen scavenger program.

Other organic chemicals can break down to organic acids in the superheater. Excessive levels of neutralizing amines should be avoided.

## 12.0 Glossary

Air handler: the mechanical portion of a HVAC system, which circulates air over the heat transfer coils and through the space to be heated or cooled

Alkalinity: a measure of the ability to neutralize hydrogen ion (acidity). In most cases alkalinity is equal to the bicarbonate, carbonate and hydroxide content of the water; it may also include phosphate species. Bicarbonate alkalinity breaks down in a boiler to carbonate, carbon dioxide, and hydroxide

Amine: a chemical characterized by having as its primary functional group a nitrogen atom attached to at least one carbon atom; used for neutralizing acidity, especially carbon dioxide from the breakdown of alkalinity

Attemperator: a section of the boiler system where water is controllably injected into superheated steam to control the degree of superheat (see superheated steam)

AVT: All Volatile Treatment; internal boiler treatment involving only volatile species, especially ammonia and hydrazine

Black Liquor Recovery Boiler: in paper mills, a boiler which burns black liquor from the Kraft pulping process to generate steam for process applications and to reduce the amount of waste for discharge; prone to deposition on the fireside

Blowdown: that portion of the boiler water which is periodically removed to maintain boiler cycles; blowdown is continuous and/or intermittent, often to a blowdown flash tank for heat recovery

Boiler: in general a piece of equipment consisting of a combustion chamber and a water-containing chamber for the purpose of converting water to steam and for its control and conditioning for a specific service

Boiler feed pump: the feed pump that pressurizes the preheated feedwater for entry into the boiler section

Boiling: the conversion of liquid to its vapor at the ambient pressure

Boiling point: the temperature at which boiling occurs at a stated pressure

BTU: British Thermal Unit; the amount of energy needed to raise one pound of water one degree F at the freezing point of water

Buffer: a chemical system that mitigates the effect of adding acid or caustic to a water; a weak acid or base is partially neutralized with a strong base or acid to form a salt of a weak acid or base. The addition of acid or base will titrate the salt without producing a large shift in pH as long as the buffer capacity has not been exceeded

Carryover: liquid water which exits the boiler; it carries all the dissolved solids that are present in the boiler water; generally undesirable; it is produced by poor water/steam separation in the steam drum due to any of a variety of causes

Chelant: a chemical that forms complexes with inorganic metal ions by attachment with two or more chemical bonds; this gives it unusually high stability; chelants often, but not always produce soluble species

Combined Cycle: a power plant design that produces electrical energy by the combination of a gas turbine (jet engine) and steam produced by recovering the waste heat of the turbine exhaust in a heat exchanger for operating a steam turbine; some of the steam is used to control the formation of $NO_x$ gases in the gas turbine

Condensate: condensed steam that may be returned to the feedwater loop of the boiler circuit

Condensate polishing: the process of removing contaminants from condensate by a combined filtration and ion exchange process.

Condensate return: that fraction of steam that is returned as condensate to the boiler; including extraction steam

Condenser: a heat exchanger designed for condensing steam to water; to minimize the high heat fluxes, it typically has a higher surface area than a liquid-liquid heat exchanger

Condenser storage tank: a storage tank for condensate from returned steam, typically vented

Conductivity: a property of materials, in this case especially water, which characterizes its ability to conduct an electric current; arising form the presence of dissolved solids which dissociate into ions

Coordinated phosphate: a boiler treatment approach requiring very pure water based on the control of a buffer condition in the sodium-phosphate equilibrium

Corrosion: in general the destruction of materials by environmental and operating factors; in particular any of a number of electrochemical, mechanical, or electro-mechanical processes which result in the transformation of a reduced metal to an oxidized state

Corrosion inhibitor: a chemical substance, which when added in minute quantities to the system substantially reduces the rate of corrosion or eliminates a particular form of corrosion such as pitting

Critical point: the pressure at which the density of the vapor and liquid phase of a pure component are equal, resulting in the disappearance of a phasae boundary; characterized by a critical pressure and a critical specific volume (the reciprocal of the density), for water $T_c$= 705.47$^0$F, and $P_c$ = 3208.2 psia, and $V_c$ = .05078 ft$^3$/lb

Cycles: the ratio of the concentration of a non-volatile dissolved species in the boiler liquid to that in the feedwater liquid; a measure of the degree of concentration

Deaerator: a device for the mechanical removal of dissolved gases, especially oxygen, in boiler feedwater; functioning on the principle of reduced solubility of most dissolved gases as temperature increases, and providing for a mechanical means of removing the gases from the system

Density: the mass of a substance divided by its volume, expressed in the units of the measurement

Deposit Weight Density: the mass of deposits residing on a unit area of a boiler tube as determined by any of a variety of means; used as a measure of loss of heat transfer and as an indicator of the need to clean the boiler

Dissolved solids: non-volatile components (solutes) in a liquid phase which do not exist as a separate phase

Distribution ratio: the ratio of the concentration of a volatile species in the steam phase to the concentration of that component in the liquid phase

Downcomer: a pipe leading from the steam drum to the mud drum or bottom header of a boiler and outside the heated portion of the boiler; it provides for the circulation of liquid in the boiler

Drum steam: the steam contained in the drum, i.e., saturated steam, also containing physically entrained water

Drying drum: in a paper mill, a team heated hollow roller used to deawater the paper web after the couch and felt sections of the paper machine

Economizer: the last section of the feedwater loop just before the feedwater enters the boiler; a high efficiency heat exchanger, which utilizes waste heat from flue gases to preheat the feedwater

Efficiency: a measure of the amount of useful work obtainable from a given amount of energy input; in a boiler a complex calculation expressing the ratio of all useful extracted energy to the sum of all energy inputs

Energy: in physics the scalar (non-directional) product of force and distance; a measure of the capacity of a system to do useful work; often expressed as enthalpy or heat value in BTU's

Enhanced tubing: rifled, grooved or convoluted tubing which improves heat transfer by creating turbulence in the liquid flow, thereby decreasing the stagnant boundary layer thickness of the tube/liquid interface

Enthalpy: the energy content at constant pressure; a measure of the heat energy exchanged in a given process, such as the enthalpy of vaporization

Enthalpy of vaporization: the heat needed to change a unit mass of a liquid to its vapor at constant temperature

Expansion tank: a ballast tank, which allows for volume changes in the water contained in a hot water heater (boiler) so as to prevent water hammer, and allow for the controlled flow of the hot water

Extraction steam: steam used for process or for preheating boiler feedwater as opposed to process steam, which is used for direct heating or distillation (i.e., injection steam)

FDA: the U.S. Food and Drug Administration; a regulatory body which, among other things, sets limits on allowable concentrations of various substances in steam used for food, air conditioning/heating or pharmaceutical applications, or packaging which may contain such products

Feedwater: water which has been conditioned for entry into the boiler; usually chemically treated and heated to near boiling temperature at the throttle pressure of the boiler

Feedwater heater: a shell and tube heat exchanger using extractions steam as the working fluid

Field-erected boiler: a boiler, which is constructed on site by joining prefabricated components; usually a high capacity and/or high-pressure boiler

Filming amine: an organic chemical used for corrosion control in steam lines which functions by adsorption at the tube wall to form a hydrophobic film; typically an amine of a long chain organic group, such as octadecyl amine (ODA) $C_{18}H_{37}NH_2$

Fire tube boiler: a boiler design in which the heat source resides inside a bank of tubes, and the boiler water is on the shell side of the Enter the price per unit

Flash tank: a pressure vessel used to receive condensate at a pressure below that of its boiling point for the given temperature of the liquid; used to extract energy from a waste stream such as blowdown, thereby increasing the efficiency of the boiler

Fossil fuel: a substance that is burned to create the heat source for the boiler, consisting of hydrocarbons in the form of coal, oil, or natural gas; presumed to be formed by the transformation of plant or animal matter under reducing conditions within the earth.

Hardness: ions of polyvalent metal atoms, which form insoluble species with carbonate; usually expressed as $CaCO_3$ equivalent

Heat exchanger: a mechanical device for the transfer of heat energy from one phase to another, usually a shell and tube container in which both process and working liquids are circulated in separate spaces separated by a metallic conductor

Heat flux: the measure of the amount of heat transfer across a unit area in a unit of time, e.g., BTU/$ft^2$-sec

Heat of vaporization: see enthalpy of vaporization

Heat recovery steam generators (HRSG): a boiler-like device which uses exhaust gasses from a gas turbine to generate steam to drive a turbine used for electricity generation

Heat transfer: the process by which energy, in the form of heat, is conveyed from one phase to another, as by conduction in a heat exchanger; heat is transferred from the medium at higher temperature to the medium at lower temperature

Hideout: a phenomenon in which a chemical species decreases in concentration in a manner associated with precipitation onto the surfaces of the vessel so that it is not analytically detectable in the water phase, but has not actually left the system; especially with regard to phosphate treatments in demineralized water

Hot water heater: a device for producing hot water from slightly below to slightly above atmospheric boiling temperature, comprising a heater section, expansion tank, and piping and valving for water distribution

Humidification: the process of adding moisture content to air by using steam or hot water, and injecting the vapor into an air handler

HVAC: Heating Ventilation and Air Conditioning

Injection steam: steam that directly contacts the process as opposed to indirect heating via a heat exchanger

Internal treatment: chemical treatment added to the boiler as opposed to the feedwater or condensate; usually a precipitating treatment, chelant, all polymer, combination, or coordinated phosphate

Load: the process using the steam, such as a turbine or cooker, etc.

Makeup: any fresh water added to the boiler circuit to make up for losses due to blowdown or non-returned steam; usually added to the steam drum

Mud drum: in many boilers a lower drum intended to promote circulation in the boiler and to entrain suspended solids; these drums have fewer internal elements than a steam drum and are usually flooded; the drum at the cold end of the downcomer

Natural circulation: boiler circulation effected solely by the density difference between cold, steam free boiler water and hotter, steam containing water

Nuclear fission: a heat source for electrical power boilers derived from the process of atomic disintegration in a nuclear reactor

Oxygen scavenger: a chemical substance that is capable of reacting with oxygen under feedwater conditions so as to reduce the level of dissolved oxygen below that achievable by mechanical deaeration

Package boiler: a boiler that is constructed in a shop and is shipped and installed as a single, integrated boiler system; usually confined to lower pressures and steam rates below about 45,000 pounds per hour

Pascal: a unit of pressure; one pascal equals 0.101 atmosphere or 0.0069 psi

Passivation: the process whereby a metal is converted to a passive phase; such as iron to magnetite

pH: shorthand for "Power of Hydrogen"; the negative of the logarithm (base 10) of the molar concentration of hydrogen ion

Phase: a form of matter characterized by having continuous properties such as density and composition; e.g., the liquid phase of water

Polymer: a chemical substance characterized by the presence of a large number of repeating units; in water treatment polymers are used for dispersion or flocculation

Ppb: part-per-billion; one microgram per liter equals one ppb

Ppm: parts-per-million; one milligram per liter equals one ppm

Psia: pounds per square inch absolute; a unit of pressure not corrected for ambient pressure

Psig: pounds per square inch gauge; a unit of pressure, which is the difference between the internal pressure, and the ambient pressure, but most often the ambient pressure correction is taken as one standard atmosphere (14.7 psi)

Riser: a tube carrying boiler water to the steam drum

Saturated steam: steam that is at the vapor pressure of water at that temperature; any lowering of the temperature or raising of the pressure will result in the formation of some liquid phase

Steam: the gaseous phase of water

Steam drum: the boiler element consisting of a horizontal metal tube with risers, a downcomer, internal elements for chemical treatment addition, makeup water addition, level control, and a steam exit; used to promote efficient separation of the steam from the water in a boiler

Steam generator: a vessel in which steam is produced by a liquid/liquid or gas/liquid heat exchange as opposed to direct firing

Steam purity: the attribute of steam that expresses the fraction of contaminants in the steam

Steam quality: the attribute of steam that expresses the fraction of liquid moisture in the steam

Steam separator: an element of the steam drum, as baffles or a venturi element used to effect separation of the steam from physically entrained water droplets; used to enhance steam quality and steam purity

Steam table: a compilation of steam properties such as pressure, enthalpy, and specific volume as a function of temperature

Stoichiometry: the relationship of reacting quantities and product quantities (mass, moles, equivalents) of components in a chemical reaction

Supercritical steam: steam that is above its critical temperature or pressure

Superheated steam: steam that is not in equilibrium with the liquid phase; the temperature may be lowered or the pressure raised to some extent without the appearance of any liquid phase; used in most systems to prevent condensation of moisture in the steam line prior to its end use

Superheater: a boiler element used to add heat to saturated steam after it exits the boiler so as to raise the steam above the saturation point temperature for that pressure

Throttle pressure: the pressure of the steam after it exits the boiler and any superheaters as required by the process or design of the steam distribution system

Transport: the movement of contaminants, such as corrosion products, from the feedwater system to the boiler

Turbine: a mechanical device for converting heat energy of steam to mechanical energy of rotation

Vapor pressure: the absolute pressure of the gaseous phase of a pure component in equilibrium with its liquid phase at a given temperature

Water hammer: an undesirable effect of sudden changes in flow rate or direction caused by improper design of the piping system; it can cause physical damage to the piping and valves in such a system

Water tube boilers: boilers in which the water flows within the tubes, and the heat source is external to the tubes.

## 13.0 Technical References

NACE Bibliography of Pictorial References Concerning Boiler Tube Failures, TPC 14, National Association of Corrosion Engineers, Houston, TX.

NACE Corrosion Failures in Boilers, TPC 17, National Association of Corrosion Engineers, Houston, TX.

NACE Water Wastewater CICS Corrosion Control in Steam Generating Systems, National Association of Corrosion Engineers, Houston, TX.

ABMA #101, Handbook of Power, Utility and Boiler Terminology and Phrases, American Boiler Manufacturers Association, American Boiler Manufacturers Association, 4001 North 9th Street, Suite 226, Arlington, Virginia 22203-1900

ABMA #300 Performance Guidelines for HRSG Units, American Boiler Manufacturers Association, 4001 North 9th Street, Suite 226, Arlington, Virginia 22203-1900

ABMA #400 Water Requirements for Water Tube Boilers, American Boiler Manufacturers Association, 4001 North 9th Street, Suite 226, Arlington, Virginia 22203-1900

ABMA #503, The Boiler Book, American Boiler Manufacturers Association, 4001 North 9th Street, Suite 226, Arlington, Virginia 22203-1900

ASHRAE, HVAC Applications Handbook, American Society of Heating, Refrigeration, and Air-Conditioning Engineers, American Society of Heating, Refrigerating and Air-Conditioning Engineers, Inc. 1791 Tullie Circle, N.E., Atlanta, GA 30329

D. Gunn and R. Hortons, Industrial Boilers, Longman Scientific Technical, London, 1989

Boilers, Evaporators and Condensers, S. Kakac, ed., Wiley, New York, 1991

P. Cohen, ASME Handbook on Water Technology in Thermal Power Systems, American Society of Mechanical Engineers, New York, 1989

H.H. Uhlig, Corrosion and Corrosion Control, Wiley, New York, 1985. Second Edition edited by R. Winston Revie, 2000.

G.T. Upperman, Water Analysis Manual for Fossil Fuel Fired Boilers, WCG:91:1078-5, Babcock and Wilcox Company, Barberton, OH, 1991

E. Nordell, Water Treatment for Industrial and Other Uses, 2nd ed., Reinhold Publishing Corp., New York, 1961

R.E. Hall, Phosphate in BoilerWater Conditioning, Journal of the American Water Works Association, 21(1), 79, 1929

District Heating Handbook, 4th ed., International District Heating Association, Washington, D.C., 1983

W. L. Campagne, What's Steam Worth?, Hydrocarbon Processing, August 1981, p117

A. Watson, Blowdown Heat Recovery Systems, Plant Engineering, June 28, 1984, p. 53

Power Magazine Special Report for Water Treatment for Boilers, June 1973, Power Magazine, New York

# CHAPTER 3
# TRAINING QUESTIONS

1. The steam cycle is also an energy cycle. Describe the energy changes for the feedwater, boiler and condensate (section 5.2).
2. Describe the function of makeup water (section 2.2).
3. Why is it important to minimize makeup water (section 2.2.1)?
4. Describe the function of the feedwater (section 2.2.2).
5. What is the purpose of blowdown? (section 2.2.2-3)
6. What is the relationship of feedwater rate to blowdown rate? (section 2.2.2-3)
7. Why is it important to limit blowdown? (section 2.2.2-3)
8. Describe the main performance differences between firetube and watertube boilers. (section 3.1)
9. You are taking over treatment of an "A" type water tube boiler. It has a history of failures due to overheating. What do you suspect is the problem? (section 3.2.3)
10. Describe the principle differences between a heat recovery steam generator (HRSG) and a boiler. (section 3.3.3)
11. Building heating is often supplied by cast iron boilers or hot water heaters. Why? (section 3.4.3)
12. Firetube boilers are almost always treated with sulfite. Why? (section 3.4.4)
13. Describe how natural circulation works. (section 3.5.2)
14. What is the main function of a feed water heater? (section 4.2)
15. Assume fuel costs are about $3.00 per million BTU. If a feedwater heater heats the water from 150° F to 180°F what is the savings per day for a 40,000 pph boiler operating at 20 cycles? (section 6.1-6.4)
16. A tray deaerator is rated at 7 ppb of dissolved oxygen. The feedwater exiting the storage tank has in excess of 200 ppb of dissolved oxygen. There is no chemical oxygen scavenger in use. List the possible causes. (section 4.3.4)
17. How much steam is required to deaerate feedwater at 25,000 lb/hr? The feedwater enters the deaerator at 180°F. The deaeration temperature is 215°F. (section 4.3.4)
18. What are the principal functions of the steam drum? (section 4.5.3)
19. A steam system is subject to rapid and frequent load changes (steam flow). When the load decreases, there is a surge of carryover into the steam. Why does this happen? (section 4.5.3)

20. A 10,000 lb/hr boiler operates at 20 cycles of concentration. It has 80% condensate return (CR). The makeup water has 2 ppm of total hardness. What is the feedwater hardness, and what is the boiler hardness? (section 4.8.2)
21. One boiler horsepower is defined as the evaporation of 34.5 pounds of water per hour, which is equal to 34,500 BTU/hr. How many pounds of steam per hour is produced by a 500 HP boiler operating at 150 psig?
22. Why do boiler allowable cycles generally increase with operating pressure? (section 7.6)
23. A customer has a boiler using city water for makeup, and is operating at ten cycles. He wants to save money on treatment and energy costs. How can you help him? (section 4.8.1, 6.4-6.9)
24. You are treating a 125 psig boiler using softened city water. The boiler is treated with caustic and polymer. It also uses sulfite as an oxygen scavenger. How do you determine boiler cycles?.(sections 6.3 and 6.4).
25. What is the most common treatment for low pressure boilers using unsoftened water? (section 7.2.1)
26. What is the effect of hardness in feedwater? (section 7.3)
27. What are the two main treatments for hardness? (section 7.3)
28. How much disodium phosphate (DSP.12$H_2O$) should be fed to a boiler with 3 ppm of hardness in the feedwater, and 10 cycles of concentration? (section 7.3.2)
29. With the previous program, how much polymer should be fed if the boiler conductivity is 3500 $\mu$S/cm? (section 7.3.2)
30. You want to simplify a treatment program by combining the oxygen scavenger with a phosphate product in the same day tank. Discuss. (section 7.3.3)
31. Your competitor is using a chelant program. What should you be looking for? (Sections 7.3.4 and 7.3.5)
32. A 15 psig boiler using softened city water has a feedwater total alkalinity of 6 ppm. The boiler is to be run at 20 cycles. Discuss how you would evaluate the treatment recommendation. (Sections 7.5 and 7.6)
33. A boiler operating at 90 psig has about 6 ppm of M alkalinity in the feedwater, and operates at 20 cycles. How much morpholine should be fed to the steam to neutralize the carbon dioxide, and maintain the pH around 8? (sections 7.7.3 and 7.3.1)
34. Where should the morpholine be fed? (section 7.7.3)

## Some Additional "Extra Credit" Questions

35. What is the pressure differential in a natural circulation system 100 feet high if the average densities of the supply and return water are 60 and 62 pounds per cubic feet respectively? (section 3.5.2)
36. Using the chart in Figure 3.8, what is the oxygen content in ppb leaving a deaerator operating at 6 psig (20.7 psia) and 220°F? (section 4.3.4)
37. The saturated steam in a 600 psia boiler meets purity standards, but the superheated steam has excessive impurities. Explain, and show how to correct this. (section 4.7)
38. Calculate the amount of attemperation water at 300 degrees F needed to reduce the degree of superheat from 150 to 125°F at 600 psia steam for a steam flow rate of 10,000 lb/hr. (section 4.7)
39. What is the velocity of steam flow (ft/sec) in an 8 inch ID steam line carrying 10,000 lb/hr of superheated steam at 250 psia and 550° F? (section 5.3.2)
40. In problem 26, if the velocity is too great, qualitatively explain how to reduce it. Quantitatively, reduce the velocity to 10 fps. (section 5.3.2)
41. What is potentially wrong about the previous answer?
42. In problems 26-28, how much heat must be added to achieve the desired results? (section 5.3.6)
43. From problem 16, what is the yearly cost for the previous problem?

## ANSWERS TO CHAPTER 3 TRAINING QUESTIONS

### Answer to Question 1

Feedwater absorbs energy to raise its temperature to near the boiling point at the boiler pressure. In the boiler, heat is supplied to convert the hot water to steam at the boiler pressure (heat of vaporization). In the condensate, heat is given up by the steam at the local pressure to change from a gas to a liquid (heat of vaporization). The energy liberated is used to accomplish the work required by the process.

### Answer to Question 2

Water losses in the boiler circuit occur via blowdown, non-returned condensate, deaeration steam, and other miscellaneous losses. Makeup water replaces these losses to keep the liquid level in the boiler constant.

### Answer to Question 3

Makeup water is cold and untreated. It is a load on the fuel cost and chemical treatment costs.

### Answer to Question 4

Feedwater is the water leaving the boiler feed pumps. Typically it has been deaerated and heated to near the boiler operating temperature. It functions to replace the steam and blowdown leaving the boiler.

### Answer to Question 5

As water is converted to steam in the boiler, the dissolved solids remain in the boiler water. Fresh makeup water transports additional dissolved solids into the boiler. In order to maintain a tolerable level of dissolved solids in the boiler water, a portion of that water must be removed periodically, carrying away some of the excess dissolved solids. It is replaced with makeup water at a lower level of dissolved solids.

### Answer to Question 6

The dissolved solids removed by a volume of blowdown (concentrated water) should equal the amount of dissolved solids carried into the boiler by a (larger) volume of (more dilute) feedwater in the same time period on average. Also, see chapter 4, section 3.5.3.

### Answer to Question 7

Heat value and chemical treatment are removed from the boiler by blowdown. This is a cost of operating the system. Blowdown should be limited consistent with other operating requirements on boiler chemistry.

Answer to Question 8

In watertube boilers, water flows inside the tubes and hot combustion gases flow around the tubes By contrast, in firetube boilers the water flows around the heat transfer tubes and combustion gases flow inside the tubes. Water flow velocities are lower in firetube boilers, leading to poorer heat transfer and circulation. Mixing is poorer and the fouling potential is greater. Firetube boilers are less expensive, but do not produce superheated steam. They are limited to lower pressure and steaming rate service (<300 psig, <35,000 pph).

Answer to Question 9

A type boilers have smaller mud drums, and are more susceptible to tube plugging as solids build up in the mud drum. Either bottom blows have not been sufficient, or the chemical treatment program is producing too much sludge. Start by increasing bottom blows. Also check the feedwater quality. If hardness is high consider softening or partial demineralization of the makeup water.

Answer to Question 10

An HRSG uses spent turbine gas as its heat source. The lower gas temperatures enable a lighter design for the heat transfer surfaces. Better water quality is needed because corrosion is a greater concern, and also because the intermediate pressure drum is used to supply steam for direct injection into the turbine. It must therefore be very pure.

Answer to Question 11

Answer: Often these are small systems with no capability to pre-treat the makeup water, and they can't afford a lot of chemical treatment. Cast iron boilers are very rugged, and can operate with poor quality water and minimal chemical treatment. Hot water heaters can be treated as closed systems (chapter 4).

Answer to Question 12

Usually there is no deaerator, so corrosion control is based almost entirely on oxygen control by chemical scavenging. Sulfite is the scavenger of choice for low-pressure systems due to cost, safety and ease of handling.

Answer to Question 13

Supply water is hot and less dense than the colder return water. The weight of the return column is greater per unit area than that of the supply. The pressure difference causes the water to rise in the supply tubes and descend in the return tubes. As long as the pressure differential is greater than frictional losses the water will circulate naturally.

Answer to Question 14

Feedwater heaters improve boiler efficiency. They use waste heat to preheat the feedwater. Less fuel is needed to heat the water in the boiler to the boiling point.

Answer to Question 15

1 Compute the heat savings per pound of feedwater
BTU = (180 –150)deg. F x 1 BTU/deg. F – pound = 30 BTU/lb

2. Compute the feedwater rate
S = 40,000 lb/hr, BD = 1/20 =5% of feedwater, FW =40,000 / (1-.05)
FW = 42,105 lb/hr

3. Compute the hourly BTU savings
BTU/hr = 30 BTU/lb x 42,105 lb/hr = 1,263,160 BTU/hr

4. Compute the daily BTU savings = 24 x 1,263,160 = 30.3 MM BTU/day

5. Compute the cost savings per day
$30.3 \times 10^6$ BTU/day x $\$3/10^6$ BTU = \$90.90 /day

Answer to Question 16

1. Not enough stripping steam.
2. The exit vent is too large, dropping the pressure to almost ambient. This lowers the water temperature in the deaerator
3. There are broken trays or tray supports, leading to poor equilibration with the stripping steam.
4. The feedwater is too high in oxygen for the sizing of the deaerator.
5. Calcium carbonate scale has accumulated on the trays and is blocking flow.

Answer to Question 17

1. Required steam = 1% of flow (lb/hr) for every 10°F rise
2. Steam lb/hr = 25,000 lb x (215-180)deg F x 0.01/10 deg F = 875 lb/hr

Answer to Question 18

The steam drum is primarily used to separate the steam from the boiler water. It also purifies the steam, mixes chemicals with the boiler water, accommodates changes in steam flow rates, and controls the level of water in the boiler.

Answer to Question 19

Probably a single element level controller is in use, or the steam flow element in a two element controller is malfunctioning. As load decreases, the drum level initially decreases due to the collapse of steam bubbles under higher pressure. The level controller calls for more feedwater. As the pressure equilibrates the drum level rises too high. The steam/water separation equipment cannot function efficiently if the liquid level is too high, and carryover increases.

Answer to Question 20

1. Total feedwater flow = Steam + Blowdown, Blowdown = 1/20 x FW
   FW = 10,000 + 0.05 FW, FW = 10,000 / (1-.05) = 10,526 lb/hr
2. Condensate flow = 0.8S = 8000 lb/hr (no hardness in condensate)
3. Makeup water = FW – CR = 2526 lb/hr
4. Feedwater hardness = 2 ppm x 2526/10,526 = 0.48 ppm
5. Boiler hardness = FW Hardness x Cycles = 0.48 x 20 = 9.6 ppm

Answer to Question 21

1. From the steam tables, 150 psig = 164.7 psia. The enthalpy of vaporization at 164.6 psia is 857 BTU/lb.
2. The total boiler BTU = 500 HP x 34,500 BTU/hr-HP = $17.25\text{x}10^6$ BTU/hr.
3. Total flow = $17.25\text{x}10^6$ BTU/Hr / 857 BTU/lb = 20,130 lb/hr of saturated steam.

Answer to Question 22

Generally, higher pressures require better quality feedwater to prevent corrosion and deposition problems, and also to maintain good steam purity (many impurities are more volatile at higher pressure). As feedwater quality improves, the allowable cycles can be increased. Increasing cycles conserves energy and chemical treatment.

Answer to Question 23

At 10 cycles the boiler is blowing down 10% of the feedwater. Reducing blowdown can save on energy and chemical costs. The first possibility is to use the blowdown to preheat the feedwater. Another solution is to use a flash tank to recover the heat value of the blowdown and to use the condensate for some of the makeup. This can help increase cycles by diluting the makeup water with more condensate. Softening the makeup water to remove hardness will also help in increasing cycles.

Answer to Question 24

Sodium, alkalinity, conductivity and hardness can't be used because of the chemical injection. Try using chloride or silica. Molybdate can be used as a tracer. Adding a known weight of molybdate to the boiler and measuring the resulting molybdate concentration can give a good approximation of the volume. For a better measure, determine the rate of molybdate depletion over time. See the problem in section 6.4 to apply the depletion rate equations to determine both boiler volume and blowdown rate.

Answer to Question 25

Oxygen scavenger, especially sulfite is the most common treatment. Without oxygen, corrosion rates are low. A phosphate precipitation program will be needed to control boiler deposits unless the makeup water is very soft. Chelant programs may also be used, but they are more expensive and require better control.

Answer to Question 26

Hardness will precipitate on hot surfaces as calcium carbonate scale. This can lead to corrosion, poor heat transfer, and tube overheating. Also, hardness in the feed water can result in flash precipitation in the deaerator, leading to calcium carbonate scaling in the tray section. This will reduce water and steam flow rates and prevent good dissolved oxygen removal.

Answer to Question 27

Phosphate (added as inorganic phosphate or organic phosphonate) can precipitate calcium phosphate, which is easily dispersed and removed by blowdown. Chelants, like EDTA, can complex hardness ions and keep them soluble. Chelants are less effective at higher pressure due to thermal breakdown.

Answer to Question 28

1. First establish a target phosphate residual. A reasonable value is 5 ppm as $PO_4$.
2. DSP.12W = 2.5 x FW hardness/cycles + 3.8 x target $PO_4$
   = 2.5 x 3 /10 + 3.8 x 5 = 19.75 ppm DSP, or about 20 ppm based on the blowdown rate.

Answer to Question 29

The boiler hardness is 30 ppm. This would require about 20-40 ppm polymer. But the high conductivity requires a boost in the polymer level by a factor of about 1.5, to require 30-60 ppm. The total amount will be closer to 60 ppm as active polymer.

Answer to Question 30

This is <u>not</u> a good idea. The oxygen scavenger should be fed to the feedwater. But if the feedwater has significant hardness, you can plug the line with calcium phosphate. If you want to simplify the treatment program use a chelant instead of the phosphate, and blend in some polymer for good hardness control. Then you can feed the product to the feedwater line.

Answer to Question 31

Check free chelant level and dissolved oxygen. Chelant corrosion is a very serious condition in a boiler. It can lead to rapid tube thinning. A boroscopic examination of boiler tubes can reveal the presence of chelant corrosion. Look for longitudinal grooves or gouges on riser tubes, especially on the hot side. The tubes should be shiny and wavy, with no deposition or magnetite. Run micro-hardness on the feedwater, and chelant on the boiler water. Any chelant residual in excess of 1 ppm can lead to severe boiler tube corrosion if any dissolved oxygen is present in the boiler water..

Answer to Question 32

The key question is whether caustic addition is needed. If using phosphate to treat the hardness, the pH needs to be about 11, requiring about 200-400 ppm of hydroxide alkalinity (2P-M, see chapter 1). Every 1 ppm of bicarbonate alkalinity will produce about 0.8 ppm of hydroxide alkalinity expressed as $CaCO_3$. The boiler alkalinity will be 6 x 20 = 120 ppm of bicarbonate alkalinity. This will break down to form about 95-100 ppm of hydroxide alkalinity expressed as $CaCO_3$.

About 100 to 300 ppm of additional hydroxide alkalinity as $CaCO_3$ will be needed. Caustic (NaOH) yields 1.25 ppm of hydroxide alkalinity as $CaCO_3$ for every 1 ppm of caustic (as NaOH). So from 100/1.25 to 300/1.25 ppm of caustic will be needed or 80 to 240 ppm of caustic.

Micro hardness on the feedwater or boiler water should be run to determine the feed of phosphate. Polymer can be calculated from Table 3.9 in section 7.3.2.

Answer to Question 33

Boiler M alkalinity = 6 x 20 = 120 ppm as $CaCO_3$. This will break down to form 120 x 0.79 = 95 ppm as $CO_2$. At this pressure the breakdown will only be about 50% of theoretical, or about 50 ppm of $CO_2$.One ppm of morpholine can neutralize 0.5 ppm of $CO_2$, so about 100 ppm of morpholine will be needed. This will produce a pH of just above 7, as that is the equivalence point. Add another 0.5 ppm of morpholine to reach pH about 8.5.

Answer to Question 34

Unless feedwater pH adjustment is needed, amines should be fed to the steam. This minimizes the amount of amine lost to blowdown.

## Some Additional "Extra Credit" Questions

Answer to Question 35

A one-foot high column of water will have a 2 pound/square foot pressure differential. This is 2/144 sq. in = 0.0139 psi. Atmospheric pressure is 14.7 psi. A one foot column has a pressure differential of 0.0139/14.7 = 0.0009 atm. The 100 foot high column will have a 0.09 atm. pressure differential.

Answer to Question 36

1. From the chart, the solubility of oxygen is approximately 0.5 cc/l
2. Moles of oxygen/l = 0.5 cc/l x 1 mole / 22,400 cc at STP = $2.23 \times 10^{-5}$ moles/l
3. Mass of oxygen/l = $2.23 \times 10^{-5}$ M/l x 32 g/M = $7 \times 10^{-4}$ moles/l
4. ppb of $O_2$ = $7 \times 10^{-4}$ g/l x 1 ppb / $10^{-6}$ g/l = 700 ppb

Answer to Question 37

The attemperator is drawing water from a source with excessive dissolved solids. Since the attemperator water is directly injected into the superheated steam, it will carry all of its dissolved solids. Alternatively, the steam is being superheated too much, requiring excessive amounts of attemperation water. Check on the degree of initial superheat. Switch to a source of demineralized water for the attemperator. You will need to provide a pump for this water to overcome the throttle pressure of the boiler.

Answer to Question 38

From steam tables, the enthalpy of 600 psia steam at 150 degrees of superheat is 1313 BTU/lb. 600 psia steam at 125 degrees of superheat has an enthalpy of 1297 BTU/lb. The enthalpy of 300 degree F water is 270 BTU/lb

1. The final enthalpy will be 1297 BTU/lb
2. The final steam flow will be (10,000 + X) lb/hr (X = attemperation water flow).
3. Heat and mass balance: 1313 x 10,000 + 270X = 1297 (10,000 + X)
4. Solve for X = 156 lb/hr

Answer to Question 39

1. From steam tables, the specific volume of the steam is 2.2909 $ft^3$ /lb
2. volumetric flow = 10,000 lb/hr x 1 hr/3600 sec x 2.2909 $ft^3$ /lb = 6.36 $ft^3$ /sec
3. V = flow / cross sectional area = 6.36 $ft^3$ /hr / ($4^2$ $\pi$ /144) $ft^2$ = 18.2 ft/sec

Answer to Question 40

$v = S/\rho A$, and since S and A (steam flow and cross sectional area) are fixed, we need to change $\rho$, the steam density. To decrease $v$ increase $\rho$. Since $\rho$ is the inverse of specific volume, decrease the specific volume to increase $\rho$.

$v_2/v_1 = S/\rho_2 A / (S/\rho_1 A) = \rho_1/\rho_2 = V_2/V_1$

$v_2/v_1 = 10/18.2 = 0.549 = V_2/V_1$

$V_2 = 0.549 \times 2.909 = 1.259$ $ft^3$ /lb

From the steam tables for superheated steam, 1.259$ft^3$ /lb occurs at 380 psia, between 10 and 60 degrees of superheat.

Degrees of Superheat by interpolation in the table = (1.259 – 1.2472)/(1.3606 – 1.2472) (60.39 – 10.39) +10.39 = 15.6 deg of superheat, or 380 psia at 455.2 deg. F.

Increasing the pressure for a fixed steam flow and pipe size decreases the velocity because it decreases the volume occupied by a given mass of steam.

Answer to Question 41

The amount of superheat is too low. Steam cools in the line, and may condense under these conditions. Consider increasing the superheat to at least 100 degrees of superheat. To keep the specific volume the same, we must find a new superheated steam pressure.

From the steam tables, we seek the closest match to V= 1.259 $ft^3$ /lb, and Sh = 100 degrees. The closest match is 440 psia and between 105 and 155 degrees of superheat.

The exact superheat = 105 + (155-105) [(1.259-1.2454)/(1.3319-1.2454)] = 113 degrees of superheat.

Answer to Question 42

1. Increase the temperature of the saturated steam from 250 psia (400.97$^o$ ) to 440 psia (454.03$^o$). The enthalpy change is (1204.8 – 1201.1)BTU/lb x 10,000 lb/hr = 37000 BTU
2. Superheat the 440 lb saturated steam to 113 deg of superheat:

   $\Delta H = (h_{113} - h_{sat})$BTU/lb = 1273 + (1304-1273)x8/100
   = (1276 - 1204.8)BTU/lb = 71.2 BTU/lb
3. Total superheat = 71.2 BTU/lb x 10,000 lb/hr = 712000 BTU/hr
4. Total heat input needed = 37,000 + 712,000 BTU/hr = 749,000 BTU/hr

Answer to Question 43

749,000 BTU/ hr x 24 Hr/day x 365 day/yr x $3/10$^6$ BTU = $19,700

# CHAPTER 4

# Cooling Water

## Table of Contents

# CHAPTER 4

# Cooling Water

## 1.0 Introduction

Cooling water has been called the life-blood of industry and commerce. Water is used to cool process fluids through heat exchangers; to reduce temperatures of solid products; to cool operating process equipment and machinery; to maintain temperature control in data processing centers; and to provide comfort cooling in commercial buildings, hospitals and a wide variety of other living and working spaces.

Large quantities of water are used in industry as a transport medium, for example to carry pulp in paper mills, and crushed or separated ores in the mining industry. While these are not strictly cooling water applications, transport water sometimes requires treatment similar to cooling water treatment to help prevent mineral scaling and corrosion problems.

When cooling water flows through a heat exchanger, the process is known as indirect cooling, because the water and the process fluid do not mix. Solid products may be cooled directly by spraying cooling water through nozzles. Direct cooling is common in steel mills and foundries, for example in cooling metal ingots, and in many other applications where cooling water is directed at a solid surface to remove heat.

### 1.1 COOLING SYSTEMS AND WATER USE

The majority of cooling water is used for indirect cooling through heat exchangers and condensers. Indirect cooling systems include:

- Once-through cooling water systems, in which water is taken from a source, such as a river, lake or ocean, used once by passing through a heat exchanger, or perhaps a series of heat exchangers, and returned to the source at a higher temperature.
- Open recirculating cooling systems, in which the heated water is cooled by evaporation in a cooling tower or spray pond, and reused.
- Closed recirculating cooling systems, in which circulating water is used to absorb heat in a process heat exchanger or air cooler, and is then cooled by exchanging this heat with an open cooling system in a second heat exchanger.

Roughly half of the world's available water is used for industrial and commercial cooling water. Approximately seventy percent of industrial water is used for cooling, twenty percent for process water and the remaining ten percent for other uses. Thus, the demand for cooling water has a great influence on the entire world water supply and distribution system. To reduce the water requirements for cooling systems, changes have been made to convert once-through cooling to open recirculating cooling water systems. Also, reduction of blowdown (waste water) requirements by operating at higher cycles of concentration has helped to reduce consumption of cooling water. All of these processes are explained in this chapter.

## 1.2 COOLING SYSTEM PROBLEMS AND OPPORTUNITIES

Such effective utilization of recirculating cooling water causes dissolved solids to concentrate in the water system, resulting in corrosion, mineral scale, general deposit and microbiological slime problems. Various cooling water treatment chemicals are used to help prevent these problems. The development of these chemical treatments and the related application technology provides more effective and cost-efficient utilization of cooling water.

Operational changes have also helped to conserve water. Recent developments in cooling water technology have made it possible to minimize deposition and resulting loss of thermal efficiency in heat exchangers even under severe conditions involving lower water flow rates and higher outlet temperatures. Advanced cooling water treatment technology provides energy saving to cooling systems by reducing operating demands on mechanical components such as fans and pumps.

At the same time, cooling water treatment chemicals can cause environmental pollution when they are discharged into the waterways. Many effective cooling water corrosion inhibitors and microbiocides can no longer be used because of their adverse effects on the environment. New, less polluting chemicals have been developed as replacements for these products. There is an ongoing need in the industry for water treatment chemical suppliers, venders and users to work together, to provide and properly apply more environmentally-acceptable chemical treatment programs. Again, the selection and application of chemical treatment programs in cooling water systems is a major subject in this chapter.

## 2.0 Cooling Systems Overview

### 2.1 ONCE-THROUGH SYSTEMS

Once-through cooling systems are most commonly used when adequate quantities of water of suitable quality and temperature are available. These systems were used exclusively in early plant operations and many are still found today. In these simple systems, water is pumped, or flows by gravity, from its source through heat exchangers and is then discharged. Water sources for once-through systems are usually lakes, rivers, or ocean water. A high percentage of once-through cooling water is raw (untreated) river water, chiefly because these waters are free for the pumping and are low enough in temperature to be useful for cooling.

### 2.1.1 Problems in Once-Through Systems

The major problems that develop in once-through cooling water systems are the effects of corrosion and corrosion product deposition. Mineral scale formation, water-borne solids deposition, and microbiological fouling are usually lesser problems. Once-through cooling systems are less susceptible to these problems than recirculating systems, because the residence time (holding time) of cooling water in the system is very short, the water does not concentrate, and it does not change significantly in chemical or physical characteristics.

Once-through cooling systems are now mostly found in large industrial plants and electric utility stations located on major waterways. Because of the large volumes of water that pass through these facilities, chemical treatment is mostly impractical. Corrosion problems are usually managed by choosing appropriate materials of construction (section 7). Very small dosages of phosphates and zinc may be added for corrosion control. Inexpensive dispersants are used to control deposition, plus trace amounts of oxidizing biocides. High molecular flocculants are sometime added, again at very low dosages, to reduce mud adhesion to surfaces. Chemical treatment is discussed in sections 6, 8, 9 and 10.

A unique problem that arises in both once-through and recirculating cooling systems, and also municipal water plants using river or lake water, is the presence of Asiatic clams and/or zebra mussels in the water supply. Neither of these species of mollusk is native to the United States; they were accidentally brought over in ballast water, Asiatic clams from the far east to Seattle, and zebra mussels from Russia to the Great Lakes. Both then spread rapidly around the country by attaching to the hulls of river and lake freighters and pleasure craft.

These mollusks attach themselves to water intake structures, where they grow rapidly and form large masses that interfere with water flow. Once formed, these masses are very difficult to remove. Shells can break off and plug condenser tubes. Thermal treatment and heavy chlorination are used to kill the mollusks, but they must then be mechanically removed, sometimes requiring serious interruption of water flow. Careful use of chlorine and other biocides can help to kill the mollusks in their juvenile stage, before they become attached to surfaces.

Sometimes, cooling towers are used to remove heat from once-through water before the water is discharged. Such towers are common in nuclear power plants, where the temperature rise across the condensers can be as much as 25 to 30 °F. Since the water does not concentrate, but is simply cooled and discharged, these systems do not qualify as recirculating cooling systems even though cooling towers are involved.

### 2.1.2 Cooling Lakes and Spray Ponds

Sometimes, available natural water supplies cannot provide enough water to satisfy a facility's needs for cooling water, or environmental regulations will not permit withdrawing the required amount of water. In such cases, damming up a stream or excavating a large area for holding water can create an artificial cooling lake or pond.

In this system, cooling water is discharged to the man-made cooling lake or pond, where heat is dissipated through sensible heat loss to cooler air and by evaporation. The cooled water is then re-circulated throughout the system. Makeup to the system is from rainfall and runoff, or by replenishment from a natural source, as needed. A small portion (typically less than 1%) of the cooling water is bled from the system to reduce the concentration of undesirable contaminates.

In order to speed up the cooling process, piping and nozzles or motor-driven sprayers are sometimes added to the ponds. These sprayers increase the rate of evaporation by spraying the heated cooling water into the surrounding air. These systems are referred to as spray ponds, and they enable smaller lakes or ponds to be used for cooling. Spray ponds also help to maintain aerobic (oxygen-containing) conditions in the pond water. This is important for good microbiological control (section 10).

Because most of the waste heat in simple cooling lakes is given off to the cooler air as sensible heat loss, evaporation rates are low and the dissolved solids in the water do not cycled up very much. Therefore, these systems are generally treated like once-through cooling systems. However, if the lake is used as a spray pond, for aeration and/or to increase cooling, substantial evaporation may occur. In such cases, the water may concentrate two or more times above makeup water levels, depending on blowdown rate.

A major concern with cooling ponds and lakes is the development of algae. Large water surface areas in direct sunlight, and with relatively slow circulation, encourage algae growth. Orthophosphate from chemical treatment programs and ground runoff, in combination with nitrogen compounds in the water, provide the nutrients necessary for algae development and growth.

Algae growth is seasonal. Low water temperatures and shortened sunlight hours during the winter months decrease rates of photosynthesis. As daylight lengthens and temperatures increase, photosynthesis activity accelerates and sudden rapid growth of algae can occur. This is called an algae bloom.

Also, large water bodies can contain decaying vegetation that produces odor problems and sometimes anaerobic (septic) conditions. Working to keep the shores and shallow water areas of man-made lakes clean is very helpful in maintaining good water quality in the lake.

## 2.2 OPEN RECIRCULATING COOLING SYSTEMS

### 2.2.1 Operations

With the trend continuing away from once-through cooling because of water conservation, thermal pollution and other discharge limitations, recirculating cooling systems have been established as an alternative and will continue to predominate in the future. Open recirculating cooling systems cool condensers and other heat transfer equipment directly, by evaporation. Also, closed cooling systems remove heat from process equipment and air conditioning systems, and then exchange this heat with an open recirculating system

Open recirculating cooling systems include cooling lakes or ponds (section 2.1.2) and cooling tower systems. The use of man-made cooling lakes or ponds for the discharge of heated water is a limited option given the constraints of land availability and cost. Cooling tower systems have therefore become the prevailing method of industrial heat rejection. A major advantage of cooling towers is that they reduce makeup water requirements. However, pretreatment of the makeup water (chapter 2) may be required to improve water quality. Water quality is explained in the introduction to this manual.

Cooling tower systems perform two basic functions: they collect waste heat from a process unit, condenser, or operating equipment, and they dissipate this heat to the atmosphere. Water is the medium used to collect and transport the waste heat; and water and air are the media through which the heat is dissipated. The structure in which waste heat is dissipated through evaporation and sensible heat loss is called the cooling tower. The cooled water collects below the tower in the cooling tower basin. About 80 percent of the heat exchange in a cooling tower results from evaporation, while 20 percent is transferred to the air through sensible heat. The design and operation of cooling towers is discussed in detail in section 3.0.

### 2.2.2 Problems in Cooling Tower Systems

Cooling towers concentrate water by evaporation, and therefore concentrate all of the nonvolatile constituents of the water. Cooling towers also act as efficient air scrubbers, washing out of the air any dirt, construction debris and microbiological material that may be carried into the tower. This material circulates through the system piping with the water, and concentrates in the basin along with the dissolved solids as water evaporates.

The result of all this is that careful control of cooling tower operations, and specifically designed chemical treatment programs, are required for successful operation of open recirculating cooling water systems, both large and small. Problems that must be considered include:

- Corrosion of heat exchanger tubes and condenser piping, including general surface attack, localized corrosion, and galvanic corrosion.
- Mineral scale formation on heat transfer surfaces.
- General deposition of organic and inorganic debris in the system.
- Microbiological slime formation and under-deposit microbiologically influenced corrosion (MIC).
- Algae growths in cooling towers, that restrict water flow and provide shelter and nutrients for bacteria.
- Pathogenic bacteria that can be transmitted through cooling tower sprays and aerosols, particularly legionella bacteria.

These problems lead to metal failures, reduced water flow, and reduced heat transfer capability. Fortunately, problems from all of these sources can be prevented with proper control of tower operations and good water treatment programs. These subjects are discussed in detail in subsequent sections in this chapter.

## 2.3 CLOSED SYSTEMS

Closed cooling systems recirculate the same water over and over again, using secondary heat exchangers to reject waste heat from the system. These systems are non-evaporative. Because water loss in a closed system is minor, very little makeup water is needed. Closed cooling systems are ideal for processes that require very clean, low suspended solids water, and for high purity, low dissolved solids water.

### 2.3.1 HVAC Systems

Heating, ventilating and air conditioning (HVAC) systems provide climate control for high rise office buildings, hospitals, data processing centers and countless other commercial and industrial closed environments. They also provide process cooling and refrigeration in industrial applications.

There are several different designs of HVAC machines, but they all operate on the same basic principle:

a. A closed chilled water loop circulates from the HVAC machine through large air handling units in open spaces and fan coils in individual rooms. Fans blow air over these coils and the chilled water absorbs heat, thus cooling the air. The warmed water flows back to the HVAC machine.

b. Inside the HVAC machine, a refrigeration loop absorbs heat from the chilled water, and the recooled water repeats the cycle. The heat exchanger in which this transfer of heat occurs (Section 4.0) is generally called the chiller, or evaporator.

c. Still inside the HVAC machine, the refrigerant exchanges heat with an open recirculating cooling water loop that, in turn, releases the waste heat to the atmosphere in a cooling tower. This exchange occurs in a second heat exchanger called the condenser.

The refrigeration cycle in HVAC machines (Step b above) is not discussed in detail in this manual. Basically, there are two types of machines: compression machines using Freon gas as a refrigerant, and absorption machines that use water as the refrigerant and a concentrated lithium bromide solution as the absorbent. Steam is used to evaporate the water. References at the end of this chapter provide more information on refrigeration technology.

The two heat exchangers described in steps a and c above are both shell and tube units, with water on the tube side (inside the tubes) and refrigerant on the shell side. The operating efficiency of all HVAC systems depends upon keeping these two heat exchangers clean and corrosion-free. This, therefore, becomes a major goal of every HVAC water treatment program, along with protecting the system piping. Water treatment technology is discussed in detail in sections 7 through 12 in this chapter.

### 2.3.2 Other Closed Systems

HVAC systems as described in section 2.3.1 represent the largest single use of closed cooling loops in industry and commercial buildings. There are, however, many other application of closed water systems. Following are brief descriptions of some of these applications:

Glycol systems. These are simply normal HVAC systems in which the chilled fluid is commonly a 50:50 mixture of water with either ethylene or propylene glycol for freeze protection. Propylene glycol is used where nontoxic water is required because of potential contact with food or food products, or pharmaceuticals.

Chilled water storage. This is a variant of normal HVAC operation, in which large HVAC machines are used to make chilled water during night hours when electricity rates are low. The chilled water is stored in underground tanks and used for comfort cooling during daylight hours. Another variant is ice storage, in which refrigeration machines make ice during the night hours, and the ice is then used to cool chilled water. These systems are often used in campus facilities, where chilled water must be circulated to many different, sometimes widely separated buildings.

Severe service cooling. Closed loops are used where very high heat transfer rates are involved, e.g. blast furnace cooling and continuous caster mold cooling in steel mills. Specially formulated chemicals and high dosages are required to protect these systems, and the water is often demineralized (chapter 2).

Low conductivity systems. Electric furnaces and some other industrial equipment require cooling water with very low electrical conductivity. High purity water and nonionizing organic chemicals (chapter 1) are used in these applications.

Closed heating systems. Hot water heating boilers, as described in chapter 3, are simply closed water systems in which the water is heated rather than cooled. The heat source can be a firetube boiler or a steam/water heat exchanger. Chemical treatment is generally the same as for chilled water systems, except that higher dosages are required.

Mixed piping systems. In some commercial facilities, the same air handling units and fan coils are used to supply hot air and cooled air as required. The most sophisticated systems, called "four-pipe systems" include separate supply and return piping for hot and chilled water, and separate piping inside the coils. Thus the hot water and chilled water never mix. In "two-pipe systems", the same piping is used for chilled and hot water. In these systems, the chilled and hot water mix every time operation is changed between heating and cooling. This can create special water treatment problems, so that the programs in both systems must be compatible and must work together.

### 2.3.3 Problems in Closed Systems

Closed cooling and heating systems, because they operate routinely and the water is not visible, are sometimes assumed to require less maintenance and service attention than open cooling systems. This is definitely not the case. Closed systems are the primary contact point for air in climate control systems, and they provide direct cooling of data processing equipment and process machinery. Failures in these systems can be catastrophic, and can sometimes occur quickly, without a lot of advance warning. Regular service attention to closed systems is therefore just as important as with more visible open cooling systems.

Following is a discussion of operating and water-related problems that can occur in closed water systems:

- Water quality. High quality, low suspended solids water is best for closed systems. Because makeup rates are generally very low, closed systems are normally filled with city water or another clean water supply. Suspended solids plug small water passages and form deposits on pipe surfaces that then become sites for localized, under-deposit corrosion (section 5.0). Since there is no regular bleed or blowdown from a closed system, suspended solids can accumulate in the water. Sidestream bag or cartridge filters, or sand filters in large systems, should be used wherever needed to keep closed system water clean. This is especially important in ambient cooling systems (section 2.4).

- Loss of flow. In many closed systems, there are small orifices and control valves which can easily become clogged with water-born suspended solids or corrosion products (iron oxides). This is especially important in closed systems used for precise temperature control in hospitals and data processing centers.

- Water losses. Opportunities for water losses in closed systems include:

  a. Leaking pump seals and glands.
  b. Expansion tank overflow.
  c. Leaking heat exchanger tubes and stem coils.
  d. Malfunctioning manual or automatic makeup water valves.
  e. Open drain valves and malfunctioning pressure release valves.
  f. Maintenance and construction requiring draindowns.

  If water losses are not noticed and corrected, and if chemical treatment levels are not monitored, treatments can be diluted down to ineffective levels. This can lead to the same mineral scaling, corrosion, deposition and microbiological fouling problems commonly encountered in open systems.

  Closed systems are designed to be kept clean, and do not include fouling factor allowances, as in some open systems (chapter 1). Therefore, any loss in flow or deposition on a closed system heat transfer surface will be quickly recognized as a loss in system performance. Every closed system should include a makeup water meter, and the meter should be monitored regularly. Chemical treatment must be added along with any significant amount of makeup water.

- Dissolved oxygen. So-called "tight" closed systems contain little or no dissolved oxygen, because oxygen in the water is quickly consumed by corrosion and microbiological reactions. Closed system chemical treatment programs are designed to work under these mostly anaerobic conditions. However, makeup water brings in oxygen, and pump seals can aspirate air into the system. If not detected and corrected, dissolved oxygen in a closed system can lead to catastrophic pitting corrosion of boiler tubes and system piping, and to galvanic corrosion of tube sheets in contact with copper tubes (sections 5.3 and 5.4). This can be especially serious if chemical treatments levels are allowed to drop because of high makeup water usage. Closed systems should be tested regularly for dissolved oxygen, especially if makeup usage is high or if freshly drawn water samples turn cloudy from degassing.

- Microbiological problems can be very serious in closed systems, especially if the system contains nutrients and if air inleakage and/or makeup water bring in bacteria and oxygen. Closed system microbiology is discussed in section 9.0.

## 2.4 AMBIENT COOLING (FREE COOLING)

### 2.4.1 Principles of Operation

The term "free cooling" refers to the direct addition of cooling tower water to the closed water system in which chilled water from the HVAC machine is normally circulated, thus bypassing the chiller and the associated power costs. The intended advantage of direct free cooling is to reduce the operating cost associated with the chiller during favorable conditions. During in-between seasons (spring and fall), when somewhat higher chilled-water temperatures can be maintained and when there is little need for dehumidification, the cooling tower water may be cool enough to eliminate the need for operation of the chillers and compressors.

### 2.4.2 Operating Problems

The disadvantage of direct injection of cooling water into a chilled water loop is increased corrosion and microbiological growth in the chilled water system. Chemical treatment levels in open recirculating cooling water systems are significantly lower than in closed chilled water loops, and different chemical programs are used. When the systems are mixed, the closed loop is exposed to the same conditions as in the open recirculating system. The result of this mixing is:

- Insufficient chemical treatment for closed loop operations.
- Higher levels of microbiological contamination.
- Lower concentrations of corrosion inhibitors.
- Possibly an incorrect chemical treatment program.
- Higher levels of dissolved oxygen.
- Higher levels of suspended matter.
- Higher levels of biodegradable organic matter.
- Higher mineral scaling tendencies.

Problems do not usually occur while the system is functioning in free cooling mode, with direct injection of open recirculating cooling water to the closed system. However, once the system is returned to normal operation, with mechanical cooling in operation and the open and closed loops separated,, the closed system is left filled with open system water, not properly treated for closed system operation.

The main problems that occur under these conditions are corrosion and microbiological contamination. Open system corrosion inhibitors, at normal dosages, are not able to provide corrosion protection in closed systems where dissolved oxygen levels may be low or zero (see chapter 1 and section 5 in this chapter). Under these conditions, corrosion will accelerate with the formation of tubercles (corrosion products.).

Because open system water always contains bacteria, the closed system will now be microbiologically active, with little or no microbiocide present. Anaerobic conditions will eventually occur under the growing tubercles, encouraging sulfate-reducing bacteria (SRB) and acid-producing bacteria. Both of these bacteria are associated with microbiologically influenced pitting corrosion (MIC). Refer to section 5.5.3 in this chapter for information on MIC.

The results of all this activity are, over time:

- Flow restriction in small diameter piping caused by the deposits, leading to loss in cooling efficiency, and
- Pitting corrosion failure of copper coils and steel piping due to MIC.

### 2.4.3 Chemical Treatment Options

These problems can be eliminated by retreating the chilled water with proper chemicals every time the system is returned from free cooling to normal mechanical cooling mode. However, If the system is moved to and from free cooling mode frequently (for example, daily), the cost of treating the chilled water system after each cycle can be prohibitive, especially if multiple chilled water systems are involved.

This problem may be partially eliminated if weather conditions permit leaving the system in free cooling mode for extended periods, usually several weeks at a time. With fewer free cooling cycles, the cost of chilled water treatment may be acceptable. This depends, of course, on the actual value of the electric power savings generated by using free cooling. However, it is critically important to have procedures in place to ensure that treatment is actually applied every time the chilled water system is returned to mechanical mode.

### 2.4.4 Use of Plate and Frame Heat Exchangers

The problems caused by direct injection of open recirculating cooling water into the chilled water system can be eliminated by using a plate and frame heat exchanger to separate the two systems (section 4.2.6). This isolates the condenser water from the cooling tower water while allowing heat transfer between the two water sources.

Plate and frame heat exchangers are expensive, and retrofitting a condenser water system may be difficult because of space limitations. Also, there is inevitably some loss in cooling efficiency across a heat exchanger. The cost of the installation must therefore be compared against the energy savings anticipated with the heat exchanger in place, and with the cost of chemical treatment or of simply abandoning the free cooling system.

### 2.4.5 Strainers and Filters

Most free cooling systems include large in-line strainers through which the condenser water passes when in free cooling mode. These strainers remove large particles of debris and corrosion products, but they are not designed to remove silt; finely divided corrosion products or microbiological solids.

Sidestream sand filters on both the condenser water and chilled water circuits can help to remove these small particles and thereby help to keep the systems clean. Circulation of only 3 to 7 percent of the circulating tower water flow through a side stream strainer/filter will significantly reduce maintenance costs in the open cooling tower system. This, combined with very good microbiological control in the condenser water, can help to minimize deposits and the resulting under deposit corrosion in the chilled water system during free cooling operation.

However, the installation of a sidestream filter for the cooling tower water, without microbiological control, will not reduce microbiological contamination. The filters will only remove fine particulate matter. Also, prestrainers are desirable to remove particles down to about 45 microns diameter, so that filters can more effectively remove smaller particles, down to 5 microns or lower. Self-cleaning strainers and automatic backwashing filters should be used if possible, to avoid replacing cartridges and manual backwashing.

## 3.0 Cooling Towers

As explained in section 2.2, cooling towers have become the dominant method for extracting waste heat from open recirculating cooling water systems and discharging this heat to the atmosphere. Cooling towers are built in many different designs. They range in size from small units with basin areas of only a few square feet, to the huge hyperbolic towers that dominate the landscape near nuclear power plants.

In order for an open recirculating cooling water system to operate properly and cost-effectively, the cooling tower must be able to run smoothly and continuously. It must be able to circulate the design water flow, and discharge the design heat load to the atmosphere. Therefore, one primary objective of cooling water treatment in these systems must be to help ensure that the cooling tower operates trouble-free.

This section of chapter 4 is concerned with the design and operation of cooling towers, problems that arise in cooling tower operations, and the role of water treatment programs in controlling these problems.

### 3.1 PRINCIPLES OF OPERATION

### 3.1.1 Water Flow

Cooling towers come in a variety of sizes, shapes, and construction materials, and with several different kinds of fill or packing. Regardless of the design, cooling tower operation is simple. Figure 4-1 is a schematic drawing of a typical recirculating cooling water system. The circulating cooling water, after picking up heat from process heat exchangers or HVAC chillers, passes over the cooling tower and down through the fill. The fill is designed to expose a large surface area of water. Air circulating through the fill cools the water by evaporation, and as a result of evaporation, the dissolved solids in the water become concentrated.

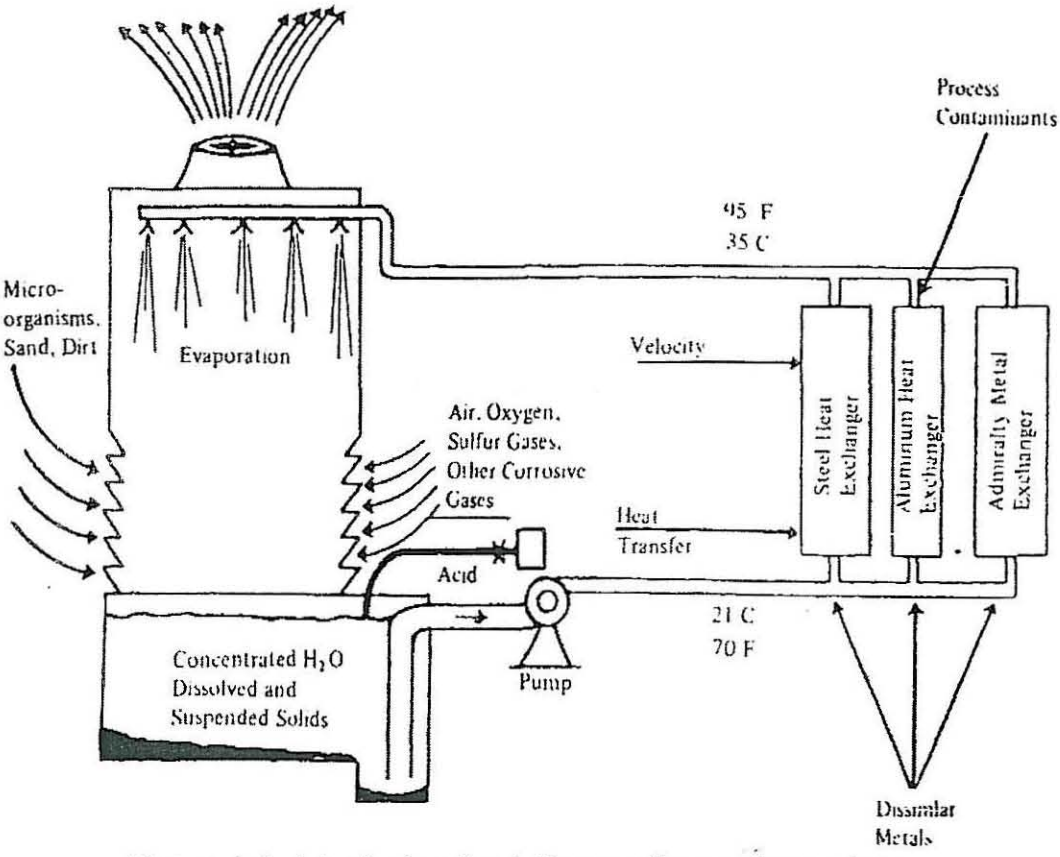


Figure 4-1. A typical recirculating cooling water system.

A water stream, known as bleedoff or blowdown, is withdrawn continuously or intermittently from the circulating water to stabilize the dissolved solids content of the water. Additional water, called windage, is lost by entrainment in the air stream, and there may also be further losses due to leaks, etc. All water lost by evaporation, blowdown, windage and other means is replaced by fresh makeup water to maintain the correct water level in the basin.

Because of the large surface area of water exposed in the cooling tower, the tower becomes an efficient gas scrubber, as shown in Figure 4-1. The water dissolves gases from the air, particularly oxygen and carbon dioxide. Carbon dioxide reacts with water to form bicarbonates and carbonates that can lead to precipitation of calcium carbonate scale, and dissolved oxygen increases cathodic corrosion reactions (chapter 1). The water also picks up wind-blown particulate matter, bacteria and nutrients for biological growth.

Thus, the combined effect of the evaporative cooling process is to increase both the corrosivity of the circulating cooling water and the tendency to form mineral scales and other tenacious deposits that can impede heat transfer and serve as sites for microbiological growth.

### 3.1.2 Makeup Water Quality

Generally there is little that can be done to control the quality of the air blowing through the cooling tower. Whatever comes along with the prevailing wind ends up in the tower. The makeup water, on the other hand, can be controlled, and proper choice and pretreatment of makeup water, if needed, can greatly improve the quality of the circulating water and the ability of the cooling system to run trouble-free.

These are primarily economic decisions. A poor quality makeup water may require low cooling tower cycles and a complex chemical treatment program. Pretreating the makeup, as described in chapter 2, to remove dissolved and suspended solids, may make it possible to operate the tower at higher cycles and with a simpler chemical treatment program, but these cost savings must be compared with the cost of pretreatment.

The nature of the facility will, to a large extent, determine the quality of raw water that can be used successfully as cooling tower makeup. As one example, consider a pharmaceutical research laboratory or a computer chip manufacturing plant. These facilities require clean conditions and precise temperature control. Little or no fouling factor allowance will be included in the design of the heat exchangers (see section 2.2.6 in chapter 1). Only clean, very low suspended solids makeup water can be used in these facilities.

Similar requirements hold for cooling systems for bank trading floors and for HVAC systems that provide comfort cooling for large commercial facilities. City water normally is satisfactory as makeup for these systems. Sometimes partial softening or demineralization (chapter 2) is used to reduce the hardness or dissolved solids level. However, if a contaminated surface or well water supply must be used as makeup water for these systems, some combination of clarification, filtration, softening or demineralization and microbiological treatment may be required.

At the other extreme, heavy industrial plants and power stations can often operate successfully with relatively poor quality makeup water. Oil refineries and chemical plants on the Mississippi River use muddy river water as cooling tower makeup, sometimes with clarification, sometimes not. Many large facilities have turned to secondary treated municipal sewage effluent as cooling tower makeup. These facilities are built with substantial fouling factor allowances, they use corrosion-resistant materials of construction, and if necessary, they operate at relatively low cycles of concentration. Restrictions on the quality of discharged air (air plume) from these towers may also limit cycles. The main considerations in water treatment in these systems is to control mineral scaling, general deposition and microbiological fouling. Towers with film-pack fill may require either pretreatment of the makeup water or special chemical treatment targeted to keeping the fill clean. See sections 3.3.2 and 3.3.3 for more on this subject.

From the water treatment point of view, it is important to understand the quality of the makeup water in specific facilities, including variability over time. Never assume, without checking, that two nearby facilities have the same makeup water supply. Water sources maybe different, and pretreatment processes, if present, may also be different.

## 3.2 TYPES OF COOLING TOWERS

Cooling towers are built in many different sizes and configurations, but they all fall into one of two design categories: natural draft towers and mechanical draft towers.

### 3.2.1 Natural Draft Towers

Natural draft cooling towers (Figure 4-2) take advantage of the temperature difference between the cool ambient air and the hotter air in the tower to create natural circulation of air through the tower structure. Warm air rising in the tower pulls cooler, ambient air from the outside into the base of the tower. Some designs, with a wide base, constricted throat and wider top, create a chimney effect. These are called hyperbolic cooling towers.

Figure 4-2. Large hyperbolic cooling towers in a power generation station..

Hyperbolic cooling towers are built large to maximize the chimney effect, and they are therefore used mostly in large industrial plants and power stations. They tend to dominate the landscape, and are often erroneously considered to be symbols, particularly of nuclear power stations. Hyperbolic towers, although used in the United States, are more common in Europe, and are frequently seen around the countryside in Great Britain, France and Germany.

### 3.2.2 Induced Draft Towers

Induced draft cooling towers involve fans in the hot exhaust air stream. These fans pull air into the tower and past the fill, and blow the hot, moist air out the stacks. Induced draft towers are built in two different configurations: counterflow and crossflow.

- In **counterflow towers** (Figure 4-3), air enters the tower through the lower air inlet area above the basin water level. The air travels vertically upward through the fill, water distribution system and drift eliminators, and out the fan stack. Hot water enters the tower through a pressure spray distribution header system near the top of the tower, and flows vertically down through the fill and into the basin.

Figure 4-3. A large induced draft counterflow cooling tower.

Counter flow cooling towers provide the most efficient use of air, because all air passes through the hottest water. Also, the finer droplet size from pressure sprays, compared to gravity flow, increases the surface area of water exposed to air in the tower. Since the distribution system is inside the cooling tower, below the mist eliminators, the counterflow design minimizes exposure of the fill and distribution system to sunlight. This reduces algae growth. However, the water distribution pressure spray system is installed in a totally enclosed tower, making the distribution nozzles difficult to inspect and maintain.

- In **crossflow towers** (Figure 4-4), air enters the tower through louvers that extend from the basin curb up to the distribution deck on the sides of the tower. Air travels horizontally through the tower fill and drift eliminators, and then vertically up through the stacks. Hot water flows across an open deck system near the top of the tower, down through distribution nozzles, and through the fill into the basin.

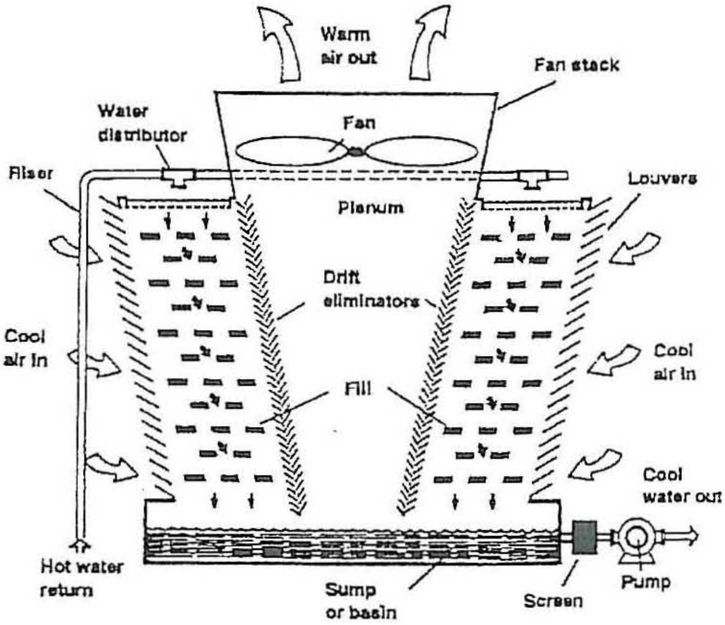


Figure 4-4. Schematic drawing of a crossflow cooling tower.

The open distribution deck in crossflow towers allows easy inspection and cleaning of nozzles. Also, the open deck accommodates changes in water flow rate with minimum change in tower pumping head. However, the open distribution deck is exposed to sunlight and thus encourages algae growth. To combat this problem, the distribution decks are often covered with removable wood or metal panels.

### 3.2.3 Forced Draft Towers

In forced draft cooling towers (Figure 4-5), fans are mounted horizontally near the bottom of the tower, above the basin. The fans push air through the fill and upwards out the stacks at the top of the tower. Hot water is distributed across the top of the fill through a pressurized spray system similar to counterflow towers.

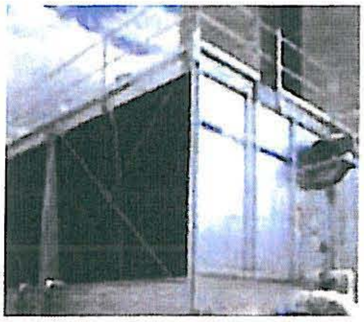


Figure 4-5. A forced draft cooling tower on a commercial building.

This design was used in many older cooling towers, and is still employed in some small HVAC towers. Forced draft towers are compact but less efficient, because it is difficult to obtain even air flow across all of the fill.

### 3.2.4 Evaporative Condensers

An evaporative condenser is an efficient design that incorporates the functions of a condenser and a cooling tower in one compact unit. To visualize an evaporative condenser quite simply, imagine a small cooling tower in which the internal fill (see section 3.3) is replaced with the tubes from a condenser, as shown in Figure 4-6. Water cascades down the tower and across the heated tubes, cooling the fluid inside by evaporation. Water flows to the basin and is pumped back to the top of the unit. The fluid inside the tubes can be steam, HVAC refrigerant or a process fluid. The tubes are not actually condenser tubes, although they serve the same function. For mechanical reasons, they are normally sections of thin wall galvanized steel pipe.

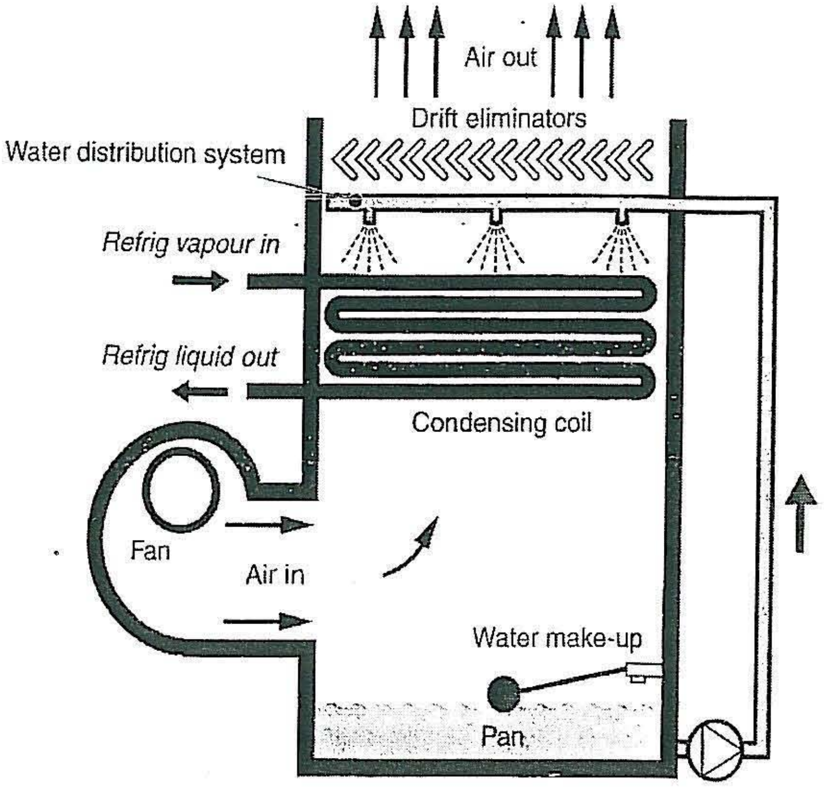


Figure 4-6.

Evaporative condensers are very common in small HVAC and refrigeration systems, as in shopping centers for example. Operation is simple and reliable. The major problems are to prevent mineral scale from forming on the tube surfaces due to evaporation of water (see section 7.0), and to protect galvanized steel from white rust and other corrosion problems (see section 6.6).

## 3.3 COOLING TOWER FILL

Fill is the internal structure in cooling towers that distributes the water throughout the tower. The purpose of the fill is to create as much water-air contact surface as possible in order to maximize both evaporative cooling and sensible heat loss. There are two types of cooling tower fill: splash fill and film fill.

### 3.3.1 Splash Fill

Splash fill was historically made from redwood slats, but is now mostly various shapes of extruded polyvinyl chloride (PVC). The shapes are designed to obtain maximum stiffness and wetted surface with minimum static air pressure resistance and minimum weight of material per square foot of wetted surface. The fill is supported by cross members in the tower, and arranged to force the falling water to bounce from slat to slat on its way down the tower. Impact breaks the water into smaller and smaller droplets, thus increasing surface area for air contact.

There are many cooling towers operating with splash fill. Many of these are being retrofitted, where possible, to use modern film fill designs (section 3.3.2). However, film fill is not suitable for all applications. Towers with poor quality, high suspended solids makeup water, and towers in which mineral scaling and microbiological fouling are difficult problems, operate better with splash fill, for reasons explained in section 3.3.2.

Even with splash fill, deposition on the slat surfaces can create serious operating problems. In addition to interfering with water flow and evaporation, the weight of the fill is a significant design factor. The fill, the attachment hardware and the water on the fill surfaces must all be supported by the tower structure. Any significant amount of deposition of any kind on the slats can increase the weight of the structure to the point that sections of film may collapse.

If deposition in the cooling tower is a problem, this must be considered when designing the chemical treatment program. Programs that can maintain clean surfaces in heat exchangers may not be sufficient to protect the tower fill. Water treatment is discussed further in section 3.3.3 and sections 8.0 to 10.0 in this chapter.

### 3.3.2 Film Fill

The most significant change in cooling tower fill in recent years has been the development and wide spread use of film-pack fill, with its higher efficiency and lower energy requirements. Film-pack fill is made of formed PVC sheets. High efficiency film fill has gained rapid acceptance in the design of industrial cooling towers due to its demonstrated performance advantage over more conventional splash bar type fills.

The main advantage of film fill over conventional tower fill is that the water is stretched or spread into a thin film as it proceeds vertically downward through the cells, where the air can effect the entire surface of the water film. Considerably more surface is then available to the flowing air for evaporation and sensible heat exchange to take place. For the same cooling parameters, this difference in mode of action can result in up to a 50% efficiency improvement over splash bar fill.

### 3.3.3 Film Fill Fouling

Film-pack fill is made from thin PVC sheets arranged in interlocking sections so that the water film must change directions several times while flowing down through the tower. For maximum efficiency, the air spaces between sheets are small. A major operating concern with film-pack fill is the ease with which the fill sections can become bridged, or plugged, with biological growth, silt and mineral scale. For this reason, film fill is not suitable for all cooling tower applications. Cooling towers using high suspended solids makeup, or that are subject to heavy microbiological fouling or mineral scale precipitation, may operate more reliably with splash fill, as discussed in section 3.3.1.

Fouling of film fill is a recognized problem in modern cooling tower operations. The general consensus is that both misuse of water – that is, operating with inadequate water quality, and design and operating problems, are responsible for the majority of film fill performance failures. Some of the identified causes of film fill fouling are:

1. Mineral scaling or precipitation on the fill sheets.
2. Suspended material such as mud, silt and corrosion product deposits becoming trapped and bridging the fill.
3. Microbiological growths of algae, bacteria, and other organisms on the fill.
4. Poor water distribution across the fill.
5. Variable water flow, resulting in low flow periods and deposits on the outer edges of the fill.
6. Combinations of all five of these mechanisms.

Studies by water treatment vendors and film fill manufacturers have confirmed that fill fouling is a site specific problem that depends on the water quality, operating procedures, water distribution and chemical treatment program.

Fouling is a general term that refers to any deposition of a foreign material on a surface, in this case the water-wetted surfaces of the fill. In most common water treatment programs, chemical programs and controls are developed to help prevent scale and deposit formation in heat exchange equipment where there are high water flow rates and velocities, heat transfer surfaces and no evaporation of water.

Because evaporation occurs at the film fill surface, standard water treatment practices may not apply. On the positive side, there are usually no direct heat transfer surfaces in cooling towers, except for evaporative condensers (section 3.2.4).

Also, the cooling effect of evaporation increases the solubility of calcium carbonate (chapter 1). However, in spite of this effect, rapid evaporation of water on the film fill surfaces can quickly cause the water-salt mixture to become supersaturated. This, together with carbon dioxide stripping that raises the local pH of the water film (chapter 1) causes calcium carbonate and other mineral salts, e.g. calcium phosphate, to become supersaturated. This leads to precipitation and deposition of salts, especially on the outside edges of the fill where evaporation rates are highest.

Another cause of mineral scaling or precipitation in the fill is lack of sufficient water flow. If water is not able to wet and flush the entire surface, deposition can occur on partially wetted surfaces. This problem often occurs when plant cooling water is "throttled" inside the plant to control process temperatures.

Other solids besides mineral scales may be involved in film fill fouling problems. Suspended solids and living microbiological matter are often the primary fouling constituents, sometimes in combination with mineral salts such as calcium carbonate, calcium sulfate, calcium phosphate, silica and aluminum salts.

Studies have shown that silt exposure alone is not often the cause of fill plugging. Microbiological growth alone can create detrimental fouling. However, the combination of silt and microbiological growth can create rapid and catastrophic fouling. Microbiological slimes (section 10.0) act as a "glue" that attracts and binds other suspended matter to the surface.

Figure 4-7. A test box containing film-pack fill.

Figure 4-7 is a photograph of a test box containing PVC film-pack fill. The box is installed in the "rain" beneath the fill in an operating cooling tower to provide a visual indication of fouling conditions in the fill.

## 3.4 COOLING TOWER OPERATIONS AND WATER TREATMENT

Proper operation and chemical treatment in cooling tower systems can do a great deal to help minimize deposition in film fill and elsewhere in the tower. Chemical treatment concepts directly related to cooling tower operations are explained in this section; details of cooling water chemical treatment are discussed in sections 7.0 through 10.0 in this chapter.

### 3.4.1 Cooling Tower Operations

Good operating practices can make a real difference in keeping cooling towers clean. Following are some good standard practices:

- Provide even water distribution from one end of the fill to the other. At least 1.5 gpm water flow per square foot of top surface area is recommended. Poorly wetted areas can provide excellent sites for microbiological organisms to grow and for silt and mineral scales to accumulate.

- Correct any sources of water carryover to eliminate unwanted water droplets outside the fill area.
- Clean distribution headers on a regular basis to insure good distribution and no dry areas.
- Replace damaged fill to prevent wet/dry areas.
- Modify the cooling tower deck and hot well to force hot water over the outer edges of the fill during periods of low flow. Some Marley towers incorporate a "dam" across the distribution deck for this purpose. Under full flow conditions, water overflows the dam and covers the entire distribution deck.

It is important to make sure that makeup water quality and the chemical treatment program in the circulating water are matched to the tower design, type of fill, heat load and operating practices in the system. Makeup water quality is discussed in section 3.1.2. Chemical treatment is discussed in section 3.4.3 and in sections 8.0 through 10.0 in this chapter.

### 3.4.2 Cooling Tower Mineral Scale and Deposit Control

Cooling water chemical treatment programs are commonly designed to control mineral scale, general deposition and microbiological problems in the main cooling system, without regard for the cooling tower. However, the condition of the tower is then used as a visual indication of system conditions. In fact, fouling conditions in the tower, particularly on the deck and in the fill, may be more severe than in the system piping and heat exchangers, so that cooling tower fouling problems do not necessarily indicate that similar problems exist in the system.

When planning a water treatment chemical program, the potential for fouling of cooling tower decks and fill should be considered. Control of cycles of concentration and pH, along with chemical treatment, should be used to support, but not replace, mechanical methods for deposit control as explained in section 3.3.3.

Chemical dispersants play a leading role in helping to keep cooling tower fill clean. Mineral scale inhibitors help to prevent scaling in heat exchangers, but scale may still form in tower fill where evaporation creates local severe supersaturation. Dispersants help to distort the resulting crystal structure, changing the scale in most cases to a less adherent sludge (section 8.5). The resulting deposits are then easier to flush from the fill surface.

Scaling processes are primarily a wet/dry interface function. Therefore when tower fill experiences extreme evaporation leading to wet/dry conditions, or when the water contains very high dissolved solids, a flush cycle for the tower fill should be considered. A flush cycle with the fans off (as often as once per 24 hours and for 2 minutes per foot of fill height) will help to flush the fill surfaces and control mineral scale and deposit buildup in the fill.

Many large industrial cooling towers are designed to be able to do what is called “zone flushing”. They can reduce water flow to selected cells and increase flow to others, to maintain cooling capacity. In effect, this provides an on-line cleaning capability for the tower fill, if the process is carried out on a regular basis.

### 3.4.3 Cooling Tower Microbiological Fouling

Cooling towers are the source of microbiological fouling in most cooling water systems. Air blowing through the tower brings in bacteria and algae, plus silt and debris that form deposits and provide “homes” for bacteria. Organisms and silt may also be carried in with surface water used as makeup. The circulating water provides dissolved oxygen and nutrients, plus a comfortable temperature and pH for microbiological growth. Sunlight promotes growth of algae on exposed decks and fill, and in wet/dry splash zones. The basin offers a safe haven for growth of both aerobic and anaerobic slimes and other deposits (section 10.0). Figure 4-8 shows microbiological slime caused by the uncontrolled growth of fungi and bacteria in a cooling water system.

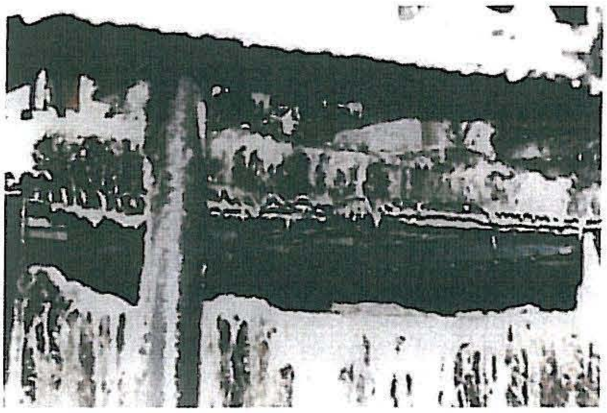


Figure 4-8. Microbiological slime in a cooling tower.

Uncontrolled growth of deposits containing microbiological matter and silt is the leading cause of plugged film-pack fill. Therefore, an effective program to control algae, bacteria, and other organisms is an essential part of any open cooling system water treatment program. In most systems operating under alkaline conditions, the microbiological control program is fundamental and should be designed first, before other parts of the program are added. This process is discussed more thoroughly in section 10.0.

Always remember that it is much simpler, more effective and less expensive to prevent problems in cooling water systems than it is to correct problems that have been allowed to develop. Cleaning is difficult, expensive, labor intensive and never acceptable as a long-term solution to fouling problems. In fact, film-pack fill that has been allowed to "bridge" so completely that water cannot flow through the fill, often cannot be cleaned and must be replaced.

An effective microbiological control program may include combinations of both oxidizing and nonoxidizing microbiocides, and biologically active surfactants called biodispersants (section 10.0). Following are some basic guidelines for controlling bacterial growth in cooling tower fill:

1. Analytically determine the nature of the fouling material and select the right combination of biocides, dispersants and mineral scale inhibitors to control the problem.
2. Provide the ability to target biocides and dispersants directly to the fill area of the cooling tower when needed. This can most easily be done by feeding chemicals, particularly oxidizing microbiocides, to the return header of the cooling tower. When this is done, the dosage must be sufficient to produce a measurable residual of each active chemical at the bottom of the fill. Chemical feed can be diverted to the return hot water header either automatically on a timed basis, or manually as needed. Chlorine or bromine usage will usually be higher under these conditions because of stripping of chlorine or bromine in the tower (see chapter 2).
3. In general, mineral scale inhibitors, dispersants and surfactants should be added continuously to the tower water. Biocides can be fed continuously or on a slug basis, as discussed in section 10.0.

Utility stations and industrial plants that discharge cooling water blowdown to a surface water source are restricted by environmental discharge permits to less than 0.2 mg/L total residual halogen (TRH) in the plant effluent. This can prevent having sufficient active halogen within the fill media. Nevertheless,, enough oxidizing biocide should be used to produce a total aerobic bacteria (TAB) count in the fill less than $10^4$ CFU/mL. In some cases, this dosage may produce a TRH level in the blowdown that exceeds the environmental discharge limitation, so that halogen removal in the blowdown may be needed (section 10.0).

A convenient way to monitor fouling of film-pack fill is to install a fill test box. This is simply a section of fill set into a framework with open top and bottom, as shown in Figure 4-7. The fill box is installed in an accessible location in the "rain" below the tower fill. The box should be inspected regularly for a "slippery" feeling and for visual evidence of deposit formation. Chemical feed to the return header can then be adjusted as needed to prevent fouling in the fill box.

### 3.4.4 Sidestream Filtration

Sidestream filtration of the circulating cooling tower water is a reliable and effective way to keep suspended solids in the water at an acceptable level.

Sidestream filtration will benefit almost any cooling tower system by helping to keep the water clear. Filtration is especially important when suspended solids rise above about 50 mg/L. OSHA, ASHRAE, CTI, AWT and other professional organizations recommend sand filtration as an effective aid in legionella bacteria control (section 9.15).

Sand filters, bag filters and cartridge filters are all effective. The choice involves site-specific decisions concerning space, manpower availability, backwash water availability, initial capital costs, etc. Multimedia sand filters are available to remove suspended solids down to 0.5 micron in diameter. Bag and cartridge filters come in a range of particle size removal down to 0.5 micron. The filter vendor should run a particle size analysis in order to recommend the appropriate media.

Sand filters can be designed to backwash automatically based on pressure drop, or on a timed basis if a pressure-based backwash does not occur at least once per day. It is important to backwash sand filters daily to prevent compaction and hardening of the filtered deposits on top of the bed. Only fresh water or cooling tower makeup water should be used as backwash water. Use of circulating tower water as backwash water can waste chemicals and lead to less effective cleaning of the bed, especially if suspended solids levels in the water are high.

Figure 4-9 shows a recommended sidestream sand filter installation. Water to be filtered is taken from the tower outlet sump, and the filtered water is returned around the outer edges of the tower basin. This provides a "sweeping" action that helps to keep solids from accumulating at low flow points in the basin.

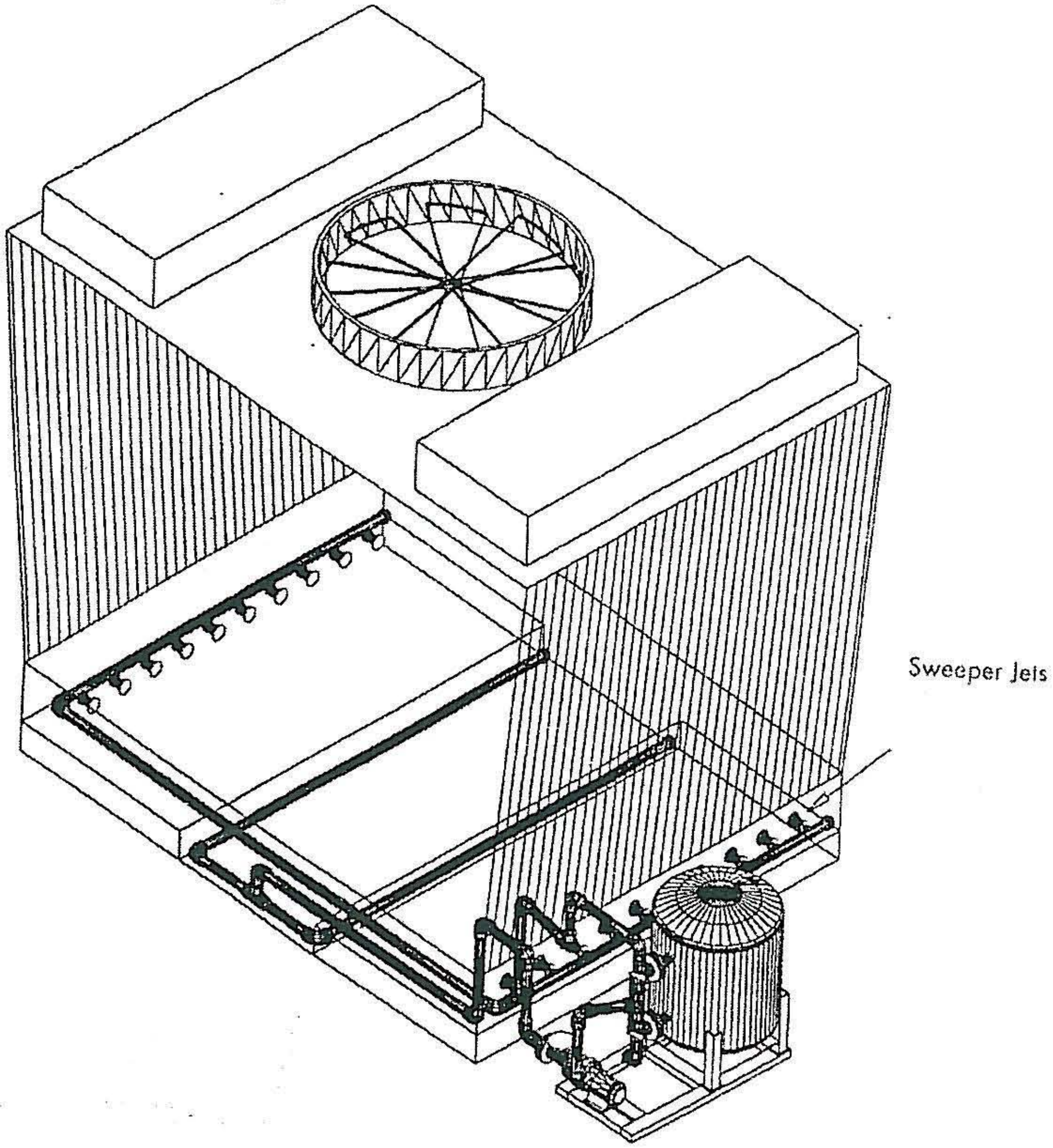


Figure 4-9. A sidestream sand filter installed with basin sweep.

Alternatively, the filtered water can be mixed with the cold water feed to the cooling system. This helps to minimize suspended solids in the circulating water. Filter sizing is usually a compromise involving efficiency, space requirements and cost of the installation. A commonly used rule-of-thumb for filter sizing is 3 to 5 percent of the circulating water flow.

## 3.5 COOLING TOWER CALCULATIONS

### 3.5.1 Thermal Performance

The following terminology and definitions apply to the thermal performance calculations in this section:

| | |
|---|---|
| WBT | Entering air wet bulb temperature. |
| DBT | Entering air dry bulb temperature. |

| | |
|---|---|
| RH | Relative humidity. |
| CWT | Cold water temperature. |
| HWT | Hot water temperature. |
| Approach | CWT – WBT, also called the approach temperature. |
| Range | HWT – CWT, also called ΔT or temperature drop. |

- The thermal performance of an evaporative cooling tower is primarily dependent upon the entering air wet bulb temperature (WBT) and relative humidity (RH). The entering WBT is an independent variable that dictates cooling tower selection. It is both the theoretical limit to the leaving cold water temperature (CWT) and the only air parameter involved in cooling tower selection.
- The difference between the CWT leaving the tower and the WBT is called the approach temperature, or approach. Approach temperatures generally fall between about 5 and 20 °F. Smaller approach temperatures mean more efficient water cooling, but require larger cooling towers. Thus a design tradeoff is involved. As the selected approach temperature is reduced, tower size and cost increase exponentially.

Measurement of the approach temperature is one way to detect possible fouling of film fill. A rising approach temperature means loss of cooling efficiency. This can have very serious consequences in terms of process operations, power generation and cooling capability. The problem should be investigated and corrected as quickly as possible.

- The range is the difference between the hot water temperature entering the tower (HWT) and the cold water temperature (CWT), that is, the temperature drop across the tower. The range is primarily affected by the design heat load and approach temperature. The range determines the amount of water evaporated as water flows through the tower. With common cooling tower designs, a good rule of thumb is: one percent of the circulating water flow rate, in gpm, is evaporated for every 10 °F ΔT across the tower.

The thermal performance of mechanical draft towers is not significantly affected by the entering air-dry bulb temperature (DBT) or the relative humidity (RH). Air mass flow is determined by the fans. However, DBT and RH do have a major effect on the performance of natural draft cooling towers. Natural draft towers depend upon the difference in densities of the ambient air entering the tower and the internal air warmed by the water being cooled, to establish air flow through the tower.

### 3.5.2 Operating Relationships

The following terminology and definitions apply to the operating relationships in this section:

| | | | |
|---|---|---|---|
| R | Recirculating rate, gpm | W | Wastage, gpm |
| $\Delta T$ | Temp. drop across tower, °F | H | Heat Dissipation, BTU/min |
| E | Evaporation, gpm | X | Cycles of concentration |
| D | Drift loss, gpm | HTI | Half-life or holding time index |
| B | Regulated blowdown, gpm | $C_m$ | Conc. of an ion in makeup |
| L | Uncontrolled leakage, gpm | $C_w$ | Conc. of an ion in wastage |
| M | Makeup, gpm | T | Tonnage rating of towers |
| V | System volume, gallon | | 1 Ton = 12,000 BTU/hr |

Using these definitions, the following relationships can be shown to exist among the operating factors in a cooling tower system:

- $E = 0\ 001 \times F_1 \times R \times \Delta T$, or $E = 0.01 \times F_1 \times R \times \Delta T/10$
  $F_1$ is a factor related to the loss of heat in a cooling tower by both evaporation and sensible heat exchange. On average, 80% of the cooling comes from evaporation, 20% from sensible heat transfer. Colder weather reduces $F_1$. Use $F_1 = 0.8$ as an average value. For rough field calculations, $F_1$ is usually ignored.
- R = Approximately 3 gpm x tonnage rating of the cooling tower.
  In HVAC systems, cooling tower tonnage will normally be 25 to 50 percent higher than the total tonnage of cooling equipment.
- $D = F_2 \times R$
  $F_2$ is a factor that varies with the age and design of the cooling tower. $F_2$ can be as high as 0.1% in old towers. In most towers today, $F_2$ averages about 0.01% to 0.03%. The value can be as low as 0.001% to 0.005% in new and well-maintained cooling towers.
- $W = D + B + L$. L is often difficult to determine and is ignored.
- $H = 8.34 \times R \times \Delta T$.
  Note: 1 ton = 200 BTU/min or 12,000 BTU/hour
- $M \times C_m = W \times C_w$.
  This assumes that the ion is not added to the system or removed from the system by other means.
- $M = E + W$, or approximately, $M = E + D + B$
- $X = MIW = C_w/C_m$, or approximately, $X = M/(B)$
- $X = 1 + E/W$, or approximately, $X = 1 + E/(B)$
- $W = E/(X - 1)$, or approximately, $B = E/(X - 1)$
- Holding time index $= 0.692 \times V/W$, or roughly, Holding time $= 0.7 \times V/B$

### 3.5.3 Sample Calculations

#### A. Evaporation

Evaporation = 0.001 x ΔT x R x 0.8

EXAMPLE: A cooling system recirculates water at 25,000 gpm. The return water temperature is 110 °F and the sump temperature is 95 °F. What is the evaporation rate?

E = 0.001 x 25,000 x 15 x 0.8 = 300 gpm

Note: The 0.8 factor in this calculation comes from the fact that only about 80 percent of the heat loss in a cooling tower comes from evaporation (see section 3.5.4). This factor is usually ignored in rough calculations.

#### B. Blowdown (Bleed)

$$\text{Blowdown (gpm)} = \frac{\text{Evaporation (gpm)}}{\text{Cycles} - 1} = E/(X-1)$$

EXAMPLE: The above system will be operated at 6 cycles. What is the blowdown rate?

BD = 300/(6-1) = 60gpm

#### C. Makeup (gpm)

The makeup water required by a cooling system is the water needed to replace the water evaporated plus the water blown down.

Makeup (gpm) = Evaporation (gpm) + Blowdown (gpm)

or

$$\text{Makeup (gpm)} = \text{Evaporation} \times \frac{\text{Cycles}}{\text{Cycles} - 1} \quad \text{or } M = E \times X/(X-1)$$

EXAMPLE: What is the makeup for the above system?

Makeup = 300 gpm + 60 gpm = 360 gpm

or

Makeup = 300 x 6/5 = 360 gpm

#### D. Holding Time Index (half-life)

The holding time index is a calculated value indicating the relative length of time that raw water makeup or added chemical will theoretically remain in the system. In actuality, the holding time index is the amount of time required to dilute the raw water or added chemical to 50% of its original concentration. The holding time index is important when selecting scale and corrosion treatments and essential when selecting biocide treatments and dosages.

The holding time index depends on the volume of the system and the blowdown rate, which in turn is a function of cycles of concentration. The calculation is:

$$\text{Holding Time (minutes)} = \frac{0.7 \times \text{Volume of system (gallons)}}{\text{Blowdown rate (gpm)}} = 0.7 \times V/B$$

EXAMPLE: The system described above has a volume of 240,000 gallons. The holding time index is:

$$\text{HTI} = \frac{0.7 \times 240{,}000}{60} = 2800 \text{ minutes} = 47.7 \text{ hours}$$

### 3.5.4 Chemical Treatment Calculations

Once the flows in the system (evaporation, blowdown, makeup and holding time index) have been calculated, chemical treatment selection, feedrates and usage calculations become simple. Basic factors required are:

- Blowdown/day = 1440 (min/day) x blowdown rate (gpm)
- 120 mg/L (ppm) = 1 lb/1000 gallons water
- Treatment required in makeup = (mg/L required in system)/cycles
- $\text{Biocide required} = \text{mg/L dosage} + \text{mg/L dosage} \times \frac{\text{(hrs contact required)}}{\text{holding time index}}$
- Acid ($H_2SO_4$) required (mg/L) = M alkalinity – M alkalinity desired

EXAMPLE: For the above system, a treatment is chosen for control of scale and corrosion. The recommended treatment is 200 to 400 mg/L to maintain a sodium molybdate concentration of 10 to 20 mg/L in the recirculating water.

- How much treatment is required on a daily basis?
  a. Daily blowdown = 60 gpm x 1440 minutes/day = 86,400 gallons/day
  b. $\text{Treatment required (average)} = \frac{300 \text{ mg/L}}{120} = 2.5 \text{ lbs/1000 gallons}$
  c. $\text{Daily requirement} = \frac{2.5 \text{ lbs.}}{1000\text{gal}} \times 86{,}400 \text{ gallons/day} = 216 \text{ lbs./day}$
- How much treatment should be added to the system to establish the initial treatment level?

  240,000 gallon volume (~10 x recirculation rate) in the system

  $$240{,}000 \text{ gallons} \times \frac{2.5 \text{ lbs.}}{1000 \text{ gallon}} = 600 \text{ lbs.}$$
- Plant personnel feel that they need to clean the system prior to starting treatment. To establish the protective film on the metal surface rapidly, you

recommend a pretreatment dose of 4 times the normal treatment level. How much treatment would be required for pretreatment?

Pretreatment dosage = 4 x 600 lbs. = 2400 lbs.

- With normal blowdown after pretreatment, approximately how long would it be before the normal treatment level was established in the system and initiation of regular chemical feed would be required?

  The calculated holding time index was 46.7 hours (approximately 2 days). Therefore, since it will take 2 days to reduce the treatment level to 50% (twice the recommended treatment level), it will take another 2 days to reduce it to the desired level. The actual formula is:

  $$\text{Desired concentration} = \frac{\text{Concentration in system}}{2 \times \text{Desired concentration}} \times \text{HTI}$$

  $$= \frac{1200 \text{ mg/L}}{2 \times 300 \text{ mg/L}} \times 2 \text{ days} = 4 \text{ days}$$

  Note: If the initial pretreatment chemicals add significantly to the conductivity of the water, and if blowdown is based on conductivity, then an adjustment must be made to avoid unnecessary blowdown and loss of pretreatment chemicals. One way to do this is to use hardness limits to control blowdown while the tower is cycling up.

- A non-oxidizing biocide is to be added to the system. The recommended minimum dosage established as required for control in this system is 30 mg/L for six (6) hours contact time. How much should be added per addition?

  $$\text{Dosage} = 30 \text{ mg/L} + 30 \text{ mg/L} \times \frac{6 \text{ hrs}}{46.7 \text{ hrs}} = 34 \text{ mg/L}$$

  $$\text{Therefore: } \frac{34 \text{ mg/L}}{120} \times 240 = 68 \text{ lbs./addition}$$

- The makeup water has an M alkalinity of 60 mg/L. It is decided to maintain the pH in the system at a control point of 7.5. How much sulfuric acid will be required?

  For rough calculations (see chapter 1), the pH-alkalinity relationship can be expressed by the equation:

  $$\text{Log M} = 0.55 \times \text{pH} - 2.27 \qquad (4\text{-}1)$$

  In the recirculating cooling water at 6 cycles, the theoretical total alkalinity will be 360 mg/L (6 x 60 mg/L) resulting in a pH of 8.8. At pH 7.5 the calculated alkalinity is 72 mg/L.

  Acid required is 360 mg/L – 72 mg/L = 288 mg/L

  $$= \underline{288 \text{ mg/L}} = 2.4 \text{ lbs/1000 gal}$$

120

Acid requirements in the makeup would be:

$$\frac{288 \text{ mg/L}}{6} = 48 \text{ mg/L}$$

$$= \frac{48 \text{ mg/L}}{120} = 0.4 \text{ lbs/1000 gal}$$

Note: Assuming that no acid or acid-producing chemicals are added as part of the treatment program, alkalinity should cycle along with non-precipitating ions such as chloride and sulfate. If cycles based on alkalinity are lower than other calculated cycle values by more than about 15 percent, this may indicate precipitation of mineral scale and the problem should be investigated (see section7.0).

### 3.5.5 System Volume Determination

There are two old rules-of-thumb used to estimate cooling system volumes:

a. V = 1.5 x basin volume

b. V = 10 x recirculating rate

These computations are useful only to obtain a preliminary estimate of the amount of salt required for a more precise determination. The protocol to determine a more precise system volume is as follows:

1. Close the blowdown
2. Estimate the volume using the above equation
3. Determine the chloride content of the tower water
4. Dissolve 50 pounds of salt for every 100,000 gallons of estimated capacity (W) Dissolve the salt in a suitable container prior to adding it to the tower basin. The solubility of NaCl is 2.9 lbs./gallon at room temperature.
5. Determine the time for the salt to be distributed throughout the system. The time is determined by dividing the estimated volume by the recirculating rate. Begin monitoring the chloride concentration every 30 minutes until two (2) successive chloride concentrations are the same. Take a minimum of three determinations over a period of 1.5 hours.
6. Determine the increase in chloride concentration ($\Delta$Cl) by subtracting the initial concentration from the peak concentration.

7. System volume (gallons) can be determined by the following calculation:

   $V = W \times (120{,}000)/(\Delta \text{Cl} \times 1.\ 65)$

8. Return the system to normal operations.

EXAMPLE:

Estimated volume = 600,000 gallons

W = (600,000/100,000) x 50 = 300 lbs. of salt

Initial Cl reading = 125 mg/L

First reading = 145 mg/L

Second reading = 170 mg/L

Third reading = 170 mg/L

$\Delta$Cl = 170 – 125 = 45mg/L

V = (300 x 120,000)/(45 x 1.65) = 485,000 gallons

## 4.0 Heat Transfer

Heat transfer and heat exchangers are covered in chapter 1, section 2.0. The present section is a review and extension of the material in chapter 1, with emphasis on cooling water heat exchangers and calculations. The reader should study chapter 1, section 2.0 before reading this section.

## 4.1 COOLING WATER HEAT EXCHANGERS

### 4.1.1 HVAC Systems

In HVAC cooling water systems, shell and tube counterflow heat exchangers with water on the tube side are the most common design. Condensers are a special case of this design, in which the shell side fluid is a condensing gas, e.g. steam or refrigerant. Evaporators are similar, except that the process is reversed. Compressed refrigerant fluid expands into the shell side of the evaporator, absorbing heat and cooling the closed loop water on the tube side.

Tubes in HVAC condensers and evaporators are almost universally made from copper, for maximum heat conductivity (section 6.0). Tubes may be smooth bore or rifled (enhanced) for better water flow and heat transfer. Air handlers and fan coils cool or warm building spaces by transferring heat to or from closed cooling water inside the tubes. These tubes are normally finned on the outside for better surface contact with air.

HVAC equipment is not designed with a significant fouling allowance, as is often the case in process heat exchangers (chapter 1, section 2.0). HVAC equipment is intended to be kept clean for maximum heat transfer efficiency. This, along with corrosion control to protect the equipment and piping, is the major challenge for water treatment in HVAC systems (see section 11.0).

### 4.1.2 Shell and Tube Process Heat Exchangers

Heat exchangers in refineries and petrochemical plants are designed to meet process requirements. High pressure process fluids, both liquid and gas, are always on the tube side, to avoid building massively thick shells. This puts cooling water on the shell side of many process heat exchangers. Fluid flow may be concurrent or countercurrent, to meet process cooling needs. Shell and tube process heat exchangers may be oriented horizontally or vertically, and in vertical units, water and process flow may be in either direction.

Similarly, process heat exchanger tube materials are usually selected with two criteria in mind: suitability for process side conditions and cost. It is then left to the water treatment vendor to design makeup water quality (chapter 2) and chemical treatment programs to protect the equipment from corrosion and keep the heat transfer surfaces clean. Chemical treatment is covered in sections 7.0 through 10.0 in this chapter.

A combination of poor heat exchanger design and operating conditions may create special challenges in water treatment. Following are some examples:

- Shell side water is difficult to treat because flow velocities are low, often less than 1 ft./sec. This allows suspended solids to settle in the system and create local corrosion cells (section 5.0). Shell side water heat exchangers often have large temperature differences between the water and process sides, and also large temperature changes from inlet to outlet. As an example, in a typical HVAC system, the tube side water temperature rise in a chiller condenser may be 10 to 15 °F, while in a refinery ethylene cooler with shell side water, the temperature rise may be 40 to 50 °F. These design factors lead to high heat transfer rates that exacerbate general deposition, mineral scaling and corrosion.
- Vertical heat exchangers represent a worst case. For process reasons, most vertical heat exchangers use shell-side cooling water. Water-borne solids tend to settle on the bottom tubesheet, creating severe corrosion problems. In an attempt to avoid these problems, some process plants operate their vertical heat exchangers with downflow water, hoping that flow velocity along the bottom tubesheet will wash away deposits. This works, but then gas pockets develop beneath the upper tubesheet, creating a different variety of corrosion problems (section 5.0). Bleed valves installed in the upper tubesheet can be used to draw away collected gas and avoid these problems.

Air bumping – that is, injecting compressed air into the water in a shell-side or vertical heat exchanger, is frequently used to create mechanical agitation and move deposits. It is very important to be sure there are no pumps or other equipment downstream from the air injection point, that can be damaged or blocked by the entrained air in the condenser water.

- Carbon steel heat exchanger tubes represent another worst case for water treatment. Corrosion creates alkaline conditions on cathodic surfaces, and this encourages calcium carbonate scale formation (chapter 1). Microbiological films (biofilms) form easily on the alkaline steel surface, and act as a "glue" to bind other deposits. All of these problems work together to foul tube surfaces. Nevertheless, because of its good heat transfer characteristics and relatively low cost, carbon steel is often the material of choice for process heat exchanger tubes. With a combination of good, design, operating procedures and water treatment, it is possible to control corrosion and fouling, and get many years of good service from carbon steel tubes.
- Low water flow, even with tube side water, creates fouling conditions. Many process heat exchangers are designed with a large built-in fouling allowance (chapter 1, section 2.0). This allows the exchanger to meet process cooling needs even with a substantial amount of deposition on the tubes. When these units are new or freshly cleaned, they are overdesigned. Tube side water heat exchangers should operate with water

flow between about 3 and 8 ft/sec. However, to avoid overcooling and losing process temperature control, operators routinely throttle the water flow, sometimes to less than 1 ft/sec. Such units often foul quickly, to the point that they cannot meet production needs even at full water flow.

These examples of heat exchanger problems illustrate, again, the importance of understanding each system thoroughly and designing water treatment programs to match system conditions. System surveys are discussed in chapter 1 and again in section 11 in this chapter.

### 4.1.3 Plate and Frame Heat Exchangers

Plate and frame heat exchangers are used frequently in the HVAC industry to separate primary from secondary chilled water systems, and chilled water from condenser water in ambient cooling systems. They are also common in process applications handling high purity fluids, or where maximum heat transfer capability is needed in a confined space.

Plate and frame heat exchangers consist of a series of gasketed, embossed metal plates arranged alternately and bolted together between end frames to form channels through which the hot process fluid and cooling water flow. The hot process fluid flows on one side of the plate while the cooling water flows on the other. The plates become the heat transfer surfaces. Because the spaces between the plates are small, most of the water is in contact with metal. Plate and frame heat exchangers have a higher heat transfer coefficient than shell and tube exchangers designed to do the same job. Also, plate and frame exchangers are typically a small fraction of the size of shell and tube units with comparable heat transfer capacity.

Plate and frame heat exchangers are usually made with stainless steel or other alloy plates, to avoid corrosion problems. Because of the narrow spacing between plates, mineral scaling and fouling must be avoided. Water flow should always be maintained above 3 ft./sec., and filtration to remove suspended solids is always recommended. Good water treatment, as discussed later in this chapter, is very important to help keep the plates clean. Flow reversal and air bumping can be used to help remove deposits. Chemical cleaning of plate and frame heat exchangers can be difficult if the plates have been bridged, and mechanical cleaning is a major project requiring disassembly of the entire unit.

## 4.2 HEAT EXCHANGER CALCULATIONS

### 4.2.1 Basic Equations

Heat transfer theory is covered in chapter 1, section 2.0. The basic equations are reviewed here in more technical terms, along with sample heat transfer calculations.

The heat transfer equation that governs a fluid being heated or cooled is:

$$q = m_w \times c_p \times (T_{wo} - T_{wi}) \qquad (4\text{-}2)$$

where $q$ = Overall heat transfer rate, or heat rate in (BTU/hr)
$m_w$ = Mass flow rate of fluid, (lbs /hr), (for water, 1 gpm = 500lbs/hr)
$c_p$ = Specific heat (BTU/lb-$^0$F), (for water $c_p = 1$).
$T_{wo}$ = Water outlet temperature, ($^0$F)
$T_{wi}$ = Water Inlet temperature, ($^0$F)

The heat given up by the shell side fluid must equal the heat taken on by the tube side fluid.

$$q_{shell} = q_{tube} \qquad (4\text{-}3)$$

$$m_{w\ shell} \times c_{p,shell} \times (\Delta T)_{shell} = m_{w\ tube} \times c_{p,tube} \times (\Delta T)_{tube} \qquad (4\text{-}4)$$

The global heat exchanger equation (chapter 1) is governed by:

$$q = U \times A \times \Delta T \qquad (4\text{-}5)$$

where $U$ = Overall coefficient of heat transfer, (BTU/hr-ft$^2$-°F)
$A$ = Surface area (external), (ft$^2$)
$\Delta T$ = Effective temperature difference, (°F)

As heat flows from the hot fluid to the cold fluid in a heat exchanger, it is opposed by 5 resistive components. These 5 resistances (modified as required to be based on the outside area), are added to obtain the total resistance to heat transfer as follows:

$$R_{total} = r_{outside\ film} + r_{outside\ fouling} + r_{wall} + r_{inside\ film} \times (d_o/d_i) + r_{inside\ fouling} \times (d_o/d_i) \qquad (4\text{-}6)$$

where $d_o$ and $d_i$ = the outside and inside tube diameters.

The resistance due to the convective heat transfer through the films, $r_{inside\ film}$ and $r_{outside\ film}$, are not usually seen as resistance, but as their reciprocals $h_i$ and $h_o$, with these known as the inside and outside heat transfer coefficients, respectively.

The term overall heat transfer coefficient, U, is used rather than total resistance. One is the reciprocal of the other

$$U = 1/R_{total} \qquad (4\text{-}7)$$

It follows from equations (4-6) and (4-7) that

$$U = 1/[(1/h_o) + r_o + r_w + (1/h_i) \times (d_o/d_i) + r_i \times (d_o/d_i)] \qquad (4\text{-}8)$$

Of the five terms in the denominator, there are usually one or two that dominate (for a particular heat exchanger in a particular mode), and therefore become more important than the others. When this dominating term is known, attention can be devoted to developing a more accurate value for it.

Often, equation (4-8) is rearranged to solve for $r_i$:

$$r_i = d_i \times [(1/U) - (1/h_o) - r_o - r_w - (1/h_i) \times (d_o/d_i)] \quad (4\text{-}9)$$

### 4.2.2 Modification For Total Fouling

The total fouling $r_{total}$ is the inside and outside fouling resistance combined. Convention has it expressed in terms of the outside surface:

$$U = 1/[(1/h_o) + r_{total} + r_{wall}\ (1/h_i) \times (d_o/d_i) \quad (4\text{-}10)$$

Equation (4-10) is then rearranged to solve for $r_{total}$:

$$r_{total} = [(1/U) - (1/h_o) - (1/h_i \times (d_o/d_i)] \quad (4\text{-}11)$$

From this equation, the fouling resistance, or fouling factor as defined in chapter 1, section 2, is defined as:

$$R_f = \text{Fouling Resistance} = (1/U_{final}) - (1/U_{clean}) \quad (4\text{-}12)$$

Another term sometimes used to evaluate heat exchangers is the cleanliness factor, $C_f$:

$$C_f = \text{Cleanliness Factor} = (U_{final}/U_{clean}) \times 100 \quad (4\text{-}13)$$

### 4.2.3 Log Mean Temperature Difference

In the global heat exchanger equation, the term effective temperature difference, $\Delta T_m$ was introduced. For the case of two fluids in either parallel flow or counter flow, the effective temperature differential is the logarithmic mean temperature difference, LMTD:

$$LMTD = \Delta T_m = (\Delta T_1 - \Delta T_2)/\ln(\Delta T_1/\Delta T_2) \quad (4\text{-}14)$$

where $\Delta T_m$ = Natural logarithmic (ln) mean temperature difference, (°F)

$\Delta T_1$ = Temperature difference (larger) of fluid at one end of the heat exchanger, (°F)

$\Delta T_2$ = Temperature difference (smaller) of fluid at the opposite end of the heat exchanger, (°F)

Not every heat exchanger is pure parallel flow or counter flow. For other type heat exchangers, LMTD Correction Factors have been empirically determined. The Tubular Exchanger Manufacture's Association has documents entitled "TEMA Standards used to correct LMTD calculations."

### 4.2.4 A Sample Calculation

A heat exchanger has just been put on line after its annual cleaning. Given the following information, calculate the overall U-value, $U_0$.

| | |
|---|---|
| Type of exchanger: shell and tube, parallel or countercurrent flow | |
| Area of heat transfer surface: | 100 $ft^2$ |
| Cooling water flow rate: | 27 gpm |

| Process liquid | Cooling water |
|---|---|
| Hot process, $T_{h,1} = 110°F$ | Cool cooling, $T_{c,1} = 85°F$ |
| Cooled Process, $T_{h,2} = 95°F$ | Hot cooling, $T_{c,2} = 95°F$ |

$\Delta T_1 = 110 - 95 = 15°F$
$\Delta T_2 = 95 - 85 = 15°F = 10°F$

LMTD = $(15 - 10)/ \ln(15/10) = 5/\ln 1.5 = 12.33°F$

Calculate the heat load, Q:

$Q = m_w \times c_p(T_o - T_i) = (27 \times 500) \times (95 - 85) = 13{,}500 \times 10$
Q = 135,000 BTU/hr

Calculate $U_0$:

$U_0 = Q/(A \times LMTD) = 135{,}000/(100 \times 12.33)$

$U_0 = 109.5$ BTU/hr-ft$^2$-°F

## 5.0 Corrosion in Cooling Water Systems

### 5.1 INTRODUCTION

### 5.1.1 Overview

Corrosion is one of four major problems that exist in open and closed cooling water systems, the other three being mineral scale formation, solids deposition and microbiological fouling. These processes are interrelated and occur together. Corroding steel surfaces are more prone to mineral scale formation; deposits create opportunities for localized under-deposit corrosion; and microbiological slimes provide the "glue" that helps bind deposits to metal surfaces and can lead to microbiologically-influenced corrosion (MIC) – see section 5.5.3.

In the years before about 1980, water treatment was a different and simpler process than it is in the twenty-first century. Environmental restrictions were not severe, and the toxic nature of many common chemicals had not been recognized. Chemical treatment of open recirculating cooling water systems in most cases involved four steps:

1. Acid addition to reduce the pH to 6.5 or below, to prevent mineral scaling;
2. Chromates, phosphates and zinc to control corrosion;
3. High doses of chlorine and toxic nonoxidizing microbiocides to control biofouling; and
4. Dispersants to control deposition of miscellaneous solids.

With increased understanding of the need to protect our environment and to avoid using toxic chemicals, water treatment has become a different and more complicated process. Chemical treatment is still very effective, but programs must be planned carefully to match the needs of each system. This requires more understanding of both the nature of the processes involved and the site peculiarities of each system.

This section discusses corrosion processes in cooling water systems. Section 6 covers the behavior of metals in cooling water, and section 7 explains mineral scale control. Later sections cover deposit control and microbiological fouling.

Corrosion of metals in water systems is an electrochemical process, involving a transfer of electrons and changes in oxidation state of the substances involved in the reaction. Electrochemical corrosion mechanisms are explained in chapter 1, section 8. The present section is a continuation of the basic information in chapter 1, with specific application to the forms of corrosion that occur on metals in cooling water systems. Chapter 1, section 8 should be read first as a basis for understanding the material in this section.

### 5.1.2 Forms of Corrosion

Corrosion can be categorized into eight different forms. Only by recognizing and understanding these forms of attack can appropriate control measures be implemented. However, in most cases, the combination of materials and the wide range of environments encountered in specific systems will result in more than one form of corrosion within a system. Even a single alloy, which can be exposed to different environments (i.e., temperatures, pH, pressures, or water qualities) can undergo more than one type of attack in a given system.

The eight forms of corrosion discussed in this section are:

1. General or uniform attack.
2. Galvanic corrosion.
3. Crevice corrosion, including differential oxygen or oxygen concentration cells, tuberculation and metal ion concentration cells.
4. Pitting corrosion, including MIC.
5. Selective leaching of metals.
6. Flow assisted corrosion.
7. Stress corrosion cracking.
8. Intergranular corrosion.

## 5.2 GENERAL OR UNIFORM ATTACK

General attack is corrosion that proceeds more or less uniformly over the exposed metal surface without appreciable localization of attack, as shown in figure 4-10. General attack is also called general corrosion, or uniform corrosion. For sheet or plate materials, this leads to relatively uniform thinning. For round bar or wires, corrosion proceeds radially inward at essentially a uniform rate around the entire circumference. The result is the production of a bar or wire of progressively smaller diameter. Pipe and tubing that suffer general corrosion are thinned from one side or the other (or both), depending on the nature of the exposure to the corrosive environment.

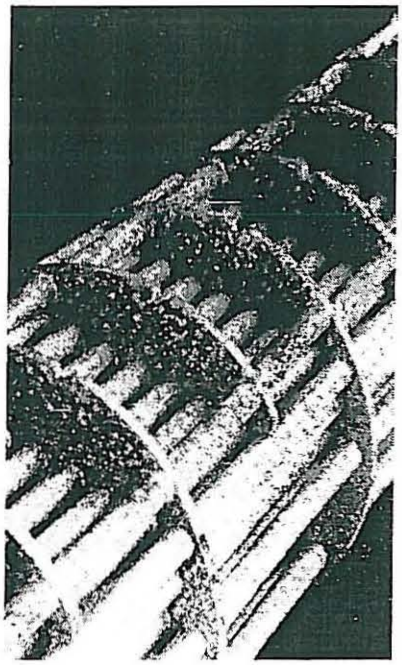


Figure 4-10. General corrosion of tube bundle baffles.

General attack can be recognized by a roughening of the surface and by the presence of corrosion products. In some cases, however, the corrosion products may not be present, as they can be soluble. Some companies define general corrosion as corrosion occurring over more than 50 percent of the metal surface, as on a corrosion coupon.

The mechanism of general attack is typically an electrochemical process, taking place on the surface of the material. The anodes and cathodes are caused by minor differences in composition or crystalline orientation between small areas on the metal surface. These sites change their position rapidly resulting in a general thinning of the metal.

Localized corrosion, the opposite of general attack, involves corrosion that occurs on selected areas, leaving other portions of the surface relatively corrosion-free. Again, some companies define localized corrosion as corrosion occurring over less than 50 percent of the metal surface. This, however, is not a specific definition. Localized corrosion is an "umbrella" term. All of the forms of corrosion discussed in this section, other than general corrosion, are forms of localized attack. Each of these is discussed separately in this section.

## 5.3 GALVANIC CORROSION

### 5.3.1 Description

As explained in chapter 1, some metals are more reactive than others. Galvanic corrosion is defined as corrosion accelerated by the potential differences between different metals when they are electrically connected and exposed to an electrolyte (cooling water.) Galvanic corrosion can also occur between a metal and an electrically conductive nonmetal such as graphite.

Corrosion products such as magnetite ($Fe_3O_4$), manganese dioxide ($MnO_2$) and sulfides can also be electrochemically active and are cathodic with respect to most metals.

Galvanic corrosion is often severe where the dissimilar materials are immediately adjacent to each other and at sharp edges or corners. A typical example is the well-known severe thread damage that can occur when a steel pipe nipple is screwed directly into a brass valve.

Ions of a more noble metal may be reduced on the surface of a more active metal (e.g., copper on aluminum or zinc). The resulting metallic deposit provides cathodic sites for further galvanic corrosion of the more active metal. Thus, for example, copper ions dissolved from heat exchanger tubing may plate out on steel piping or on a galvanized cooling tower, causing pitting corrosion.

Galvanic corrosion can be recognized by either increased corrosion of the anodic material, or decreased corrosion of the cathodic material. The electrical contact between the dissimilar materials may be through either direct contact, or an external conductive path. This is the basis for cathodic protection systems in which bars or rods of an active metal, such as zinc or magnesium, are coupled to large surfaces of a metal to be protected, such as steel water boxes in power station condensers. The potential difference between the active metal and the more noble steel causes the steel, which would normally corrode in water, to become the cathode. The steel is protected and the active anodes corrode at an increased rate. Obviously, the anodes must be replaced periodically.

### 5.3.2 The Galvanic Series

As explained in chapter 1, section 8.4, the elements in the Periodic Table (Table 1-1) can be arranged in order of their electrode potentials relative to a standard electrode, normally the hydrogen electrode. This is called the electromotive series, as shown in Table 1-11.

For practical use, commercial metals and alloys can also be arranged in order of their electrode potentials in specific environments, for example sea water. This is called a galvanic series, as shown in Table 4-1.

**Table 4-1**
The Galvanic Series of Metals in Sea Water

**Active (anodic)**

Magnesium
Zinc
Aluminum
Iron & carbon steel
Cast iron
304 & 316 stainless steels (active)
Lead/tin solder
Tin
Nickel (active)
Tin
Copper/zinc alloys (brass)
Copper
Silver solder
Nickel (passive)
304 & 316 stainless steels (passive)
Silver
Gold

**Noble (cathodic)**

The data in Table 4-1 were obtained in seawater. The order of elements can change in different environments. However, Table 4-1 has been found to be typical for cooling water environments.

Table 4-1 shows clearly why copper ions in water will plate out as metal on steel, or aluminum, or zinc, and why this can lead to pitting corrosion as discussed above. However, there are two important caveats to remember:

1. Water is necessary to complete the electrical circuit so that corrosion current can flow (chapter 1). Thus, aluminum fins are commonly attached to copper tubes in fan coils and air handlers, to increase the available surface for air-cooling. No corrosion occurs as long as the tubes are dry.
2. Metals such as aluminum, zinc and stainless steels form passive oxide coatings (chapter 1). These coatings protect the metal surface from contact with water, and thus from corrosion. For example, Table 4-1 shows that unprotected 304 and 316 stainless steels are about as active as carbon steel. However, in their normal passive state, protected by stable oxide coatings, the stainless steels are corrosion resistant. See section 5.9.3 for more information on this subject.

### 5.3.3 Forms of Galvanic Corrosion

Galvanic activity does not control the form of corrosion, which occurs at the anode; it only increases the rate of attack. The form of this corrosive attack may be general attack, pitting, or some other form of corrosion. This sometimes makes diagnosis of the source of a corrosion problem difficult. For example, if an incident of localized corrosion is diagnosed as under-deposit oxygen cell attack (section 5.4), the recommended solution might be to increase dispersant feed to help keep the surface clean. However, if the real culprit is galvanic corrosion from a cathodic source, then simply adding dispersants will not solve the problem.

Galvanic corrosion may also affect cathode sites in several ways. In general, the corrosion that would normally occur if the cathodic area were exposed to the environment by itself, will decrease when the cathode is coupled to a more active material. In some cases, however, the cathode can be adversely affected. If the environment is acid, so that the cathodic reaction is the reduction of hydrogen ions (chapter 1, section 8.3), hydrogen embrittlement, a form of corrosion discussed in section 5.11, can result.

In addition, the alkaline cathodic reaction products formed in a galvanic cell can adversely affect some materials such as aluminum and zinc. Metals that become soluble in both acidic and alkaline environments are known as amphoteric elements. The normal cathodic reaction in cooling water systems is the reduction of dissolved oxygen to form hydroxide ions (chapter 1, section 8.2). This creates a localized high pH zone at cathodic sites, that can cause corrosion of the cathode in a galvanic corrosion cell. Such attacks are called amphoteric effects. Aluminum and zinc are common amphoteric elements. Iron is also an amphoteric element, but the pH required for alkaline dissolution of iron is higher than is normally found in cooling water environments.

### 5.3.4 Area Effects in Galvanic Corrosion

Area effects in galvanic corrosion involve the relative surface areas of the cathode and anode. In cooling water, the rate-controlling reaction in the overall corrosion process is the rate of diffusion of dissolved oxygen in water to the cathodic sites at the metal surface (chapter 1, section 8.0). The rate is said to be under cathodic control, and is proportional to the cathodic area available for reduction of oxygen. Doubling the cathodic area would double the area available for oxygen diffusion, and would therefore double the corrosion rate.

On the other hand, the corrosion rate does not depend on the anodic area in the corrosion cell. The entire corrosion current generated at the cathodes is distributed over the anodic area, large or small. If the anodic area is large relative to the cathodic area, the result is general surface corrosion and the actual increases in corrosion rate may be small. Conversely, if the anodic area is small, the corrosion current concentrated at these locations can lead to deep penetration, or pitting of the metal surface. These area effects are illustrated schematically in figure 4-11. Area effects are discussed further in connection with corrosion inhibition in section 7.

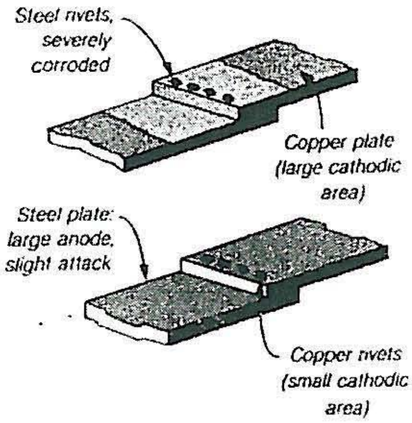


Figure 4-11. Area effects in galvanic corrosion.

### 5.3.5 Environment and Throwing Power

Water is an essential part of every galvanic corrosion circuit (chapter 1), but deionized water will not work. The water must contain dissolved ions to conduct electricity. Just as with a copper wire, the water offers resistance to current flow. The higher the dissolved ionic content of the water, the lower the resistance, or the higher the conductivity. Given the same anodes and cathodes, a high conductivity water will conduct more current and produce higher corrosion rates than a low conductivity water.

In practice, following the principle that an electric current will follow the path of least resistance, galvanic effects are usually concentrated where the anodes and cathodes are closest together. Thus, in the case of a steel nipple screwed into a brass valve, the steel threads in contact with the valve will fail, while the pipe surface just millimeters away from the valve may not be affected. The use of dielectric (nonconducting) fittings is an obvious solution to this problem.

When zinc or magnesium anodes are used to provide cathodic protection in equipment such as condenser water boxes, the designer must calculate the number, size and spacing of anodes required. This calculation involves the potential difference between the anodic and cathodic materials from Table 1-11, called the driving force, the cathodic area to be protected, and the conductivity and temperature of the water. From these variables, the designer will calculate the "throwing power" of the anodes, that is, the distance from each anode that can be protected, and hence the number of electrodes required.

Galvanic corrosion also occurs in moist atmospheric environments. Rainwater normally has low conductivity. Thus, in atmospheric exposures, resistance effects in the water limit the range of galvanic corrosion to the area where the two electrodes are in contact (when this area is filled with electrolyte) and for a very short distance around the contact area. This distance is usually on the order of 1 to 2mm.

## 5.4 CREVICE CORROSION

### 5.4.1 Definition

Crevice corrosion is a form of localized attack in which the site of attack is an area where free access to the surrounding water environment is restricted. Crevice corrosion is caused by differences in the concentrations of materials inside and outside the crevice. Therefore, crevice corrosion is also called concentration cell corrosion.

This form of localized attack can occur at crevices, where materials meet in such a way that water can enter the joint between them, but the flow of water into and out of the joint is restricted. These crevices may either be metal-to-metal or metal to nonmetal. Typical examples include poorly welded joints, improperly tightened threaded connections and gasketed flanged connections.

Crevices can also be formed under deposits of debris or corrosion products. This form of attack is called tuberculation. Because of its importance in cooling water systems, tuberculation is treated separately in section 5.5.

Crevice corrosion can be recognized by the localization of attack, either at the entrance to a crevice or deep within the crevice. When corrosion occurs deep within a crevice, it is often revealed only after a failure has occurred.

There are two basic mechanisms of crevice corrosion:

1. Oxygen concentration cells.
2. Metal ion concentration cells.

These two mechanisms are interdependent, but differ in the final manifestation of the corrosion damage.

This section discusses first the general nature of oxygen concentration cells that may appear in cooling water systems, and then metal ion concentration cells. Tuberculation is the major manifestation of oxygen concentration cell corrosion (see section 5.5).

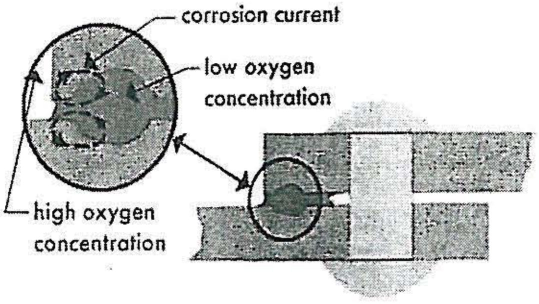
### 5.4.2 Oxygen Concentration Cells

In an oxygen concentration cell, the difference in dissolved oxygen concentration in the water between the metal areas inside and outside the crevice creates a potential difference between these areas. Oxygen concentration primarily affects the activity of the cathodic reactions involved in corrosion. Areas where the cathodic activity is high will act as cathodes with respect to areas where the cathodic activity is low. As explained in chapter 1, section 8, the most common cathodic reaction in cooling water is the reduction of oxygen:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \qquad (4\text{-}15)$$

Any increase in dissolved oxygen content in the water will tend to increase the cathodic reaction, whereas a decrease in oxygen will tend to reduce the cathodic reaction. Thus, an area with a more active cathodic reaction will tend to act as a cathode with respect to an area with a less active cathodic reaction.

Figure 4-12 is a drawing of a typical oxygen concentration cell. Because of restricted diffusion of water into the crevice and corrosion reactions inside the crevice, the water within the crevice quickly becomes depleted in dissolved oxygen. As explained above, the internal crevice area thus becomes anodic with respect to the outside area, where the higher dissolved oxygen content drives the cathodic reaction.



**Concentration cells**

Figure 4-12. Drawing of a typical oxygen concentration cell.

### 5.4.3 Metal Ion Concentration Cells

The initial driving force of an oxygen concentration cell inside a crevice causes corrosion to initiate, but that corrosion can be further accelerated by the accumulation of acidic hydrolyzed salts within the crevice. The most common manifestation of this effect is the increase in corrosion rates in concentration cells caused by chloride ions in the water. This effect is explained in detail in section 5.5.1 on tuberculation.

Another effect of increasing metal ion concentrations in a crevice corrosion cell is to actually reverse anode and cathode locations, so that corrosion occurs on the metal surface outside the crevice. Calculations from a thermodynamic equation (the Nernst equation) show that electrodes with high and low concentrations of dissolved metal ions at the electrode surface will differ in potential. The electrode with a high concentration of metal ions at the surface will have a more positive potential than the electrode with a low concentration of metal ions.

In an electrochemical cell, the surface with the more positive potential acts as the cathode. Thus, in a crevice corrosion cell, the area of the cell exposed to the high metal ion concentration that exists inside the crevice acts as a cathode with respect to the area with lower metal ion concentration outside the crevice. In metal ion concentration cell crevice corrosion, the corrosion is usually concentrated and visible at the entrance to the crevice. Crevice corrosion is clearly a complex process, with several different reactions occurring and sometimes competing. What actually happens in a given situation is site-specific, depending on the nature of the crevice, the metals involved, system design, operating conditions, water composition and chemical treatment.

## 5.5 TUBERCULATION

Tubercles are structurally complex crevice corrosion cells, in which accumulations of metal oxides (corrosion products) and other deposits cap localized regions of metal loss. Attack occurs on steel, cast iron, and rarely, on stainless steels. Tubercles may be smooth, nodular or take the form of fluted cones. Morphology depends on water chemistry, dissolved oxygen concentration, temperature, flow and corrosion rates. Differential oxygen cells fundamentally cause tuberculation. Oxygen deficient regions below the accumulated corrosion products and deposit masses produce anodic sites, while areas on top and surrounding the tubercle are cathodic.

### 5.5.1 Tubercular Structure

All tubercles have five structural features in common starting from the outside and moving towards the interior and bottom of the tubercle:

- Outer crust
- Inner shell
- Core material
- Fluid cavity
- Corroding metal floor

Tubercles grow both internally and externally. Five processes cause tubercular growth. Starting from the bottom, i.e. the corroding metal floor of the tubercle, iron metal corrodes to form ferrous ions, as in equation (4-16):

1. (Corroding floor) $Fe \rightarrow Fe^{+2} + 2e^-$ (4-16)

In the fluid cavity in contact with the metal floor, newly formed ferrous ions react with chloride ions from the water to form a weakly ionized ferrous chloride complex ion, $FeCl^+$. This complex ion then hydrolyzes (reacts with water, chapter 1) to form ferrous hydroxide and liberate hydrogen ions (acid), as in equations (4-17) and (4-18):

2. (Fluid cavity) $FeCl^+ + 2H_2O \rightarrow Fe(OH)_2 + 2H^+ + Cl^-$ (4-17)

$2H^+ Cl^- + Fe^{2+} \rightarrow FeCl^+ + 2H^+ + Cl^-$ (4-18)

Equations (4-17) and (4-18) explain why chloride ions accumulate at the bottom of growing corrosion pits and why the water in these deposits is always more acid (lower in pH) than the bulk water.

Continuing upward through the tubercle, more ferrous ions from the fluid cavity react with hydroxide ions diffusing inwards from the cathodic reduction of dissolved oxygen in the water, to form ferrous hydroxide in the core material and the inner shell, as in equations (4-19) and (4-20):

3. (Core material) $Fe^{+2} + 2OH^- \rightarrow Fe(OH)_2$ (4-19)
4. (Inner shell) $\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^-$ (4-20)

Finally, the outer crust of the tubercle is formed from the oxidation of ferrous hydroxide by more dissolved oxygen in the bulk water, as in equation (4-21):

5. (Outer crust) $2Fe(OH)_2 + H_2O + \frac{1}{2}O_2 \rightarrow 2Fe(OH)_3$. (4-21)

Ferrous ions from the core fluid also escape through tubercular fractures and are quickly oxidized to ferric hydroxide upon exposure to oxygenated water outside as in equation (4-21). The tubercular crust thus consists of large amounts of precipitated ferric hydroxide. Additionally, on top of the tubercle, hydroxide ions from equation (4-20) increase the local pH and induce precipitation of mineral scale compounds such as calcium carbonate (see section 8 and chapter 1).

Many other reactions can occur below the tubercular cap, some involving bacteria, producing siderite (ferrous carbonate, $FeCO_3$), and pyrrhotite (ferrous sulfide, FeS), as well as other compounds.

### 5.5.2 Corrosion Morphology in Tuberculation

Corroded areas beneath tubercles, in the absence of significant microbiologically influenced corrosion (MIC, section 5.5.3), are usually broad, irregular depressions. Corroded floors may be highly striated. Striations are usually associated with rapid corrosion, locally exceeding 10-20 mpy. The striations are caused by preferential attack along longitudinally oriented micro-structural features in the metal surface produced during forming or alloy manufacture. Striations are known to occur when the pH beneath the tubercle is highly acidic, and can be seen clearly after acid cleaning, but are not normally produced beneath a tubercle after an acid cleaning.

Additionally, circumferentially oriented, concentric ledges, sometime called bullseyes, may form if corrosion rates abruptly vary and continue for extended periods at the new rate. Such variations can occur, for example, during layup periods when circulation stops and dissolved oxygen levels in the water are much lower.

IMPORTANT: Not all red-brown iron oxide deposits in cooling water systems are tubercles. Even if the structure superficially resembles a tubercle, if the features described in this section are absent, the structure is not a tubercle, but rather may simply be an accumulation of deposited iron oxides and other material. Look for corrosion beneath the deposit. If there is none, the iron oxide in the deposit is probably material transferred from elsewhere in the system.

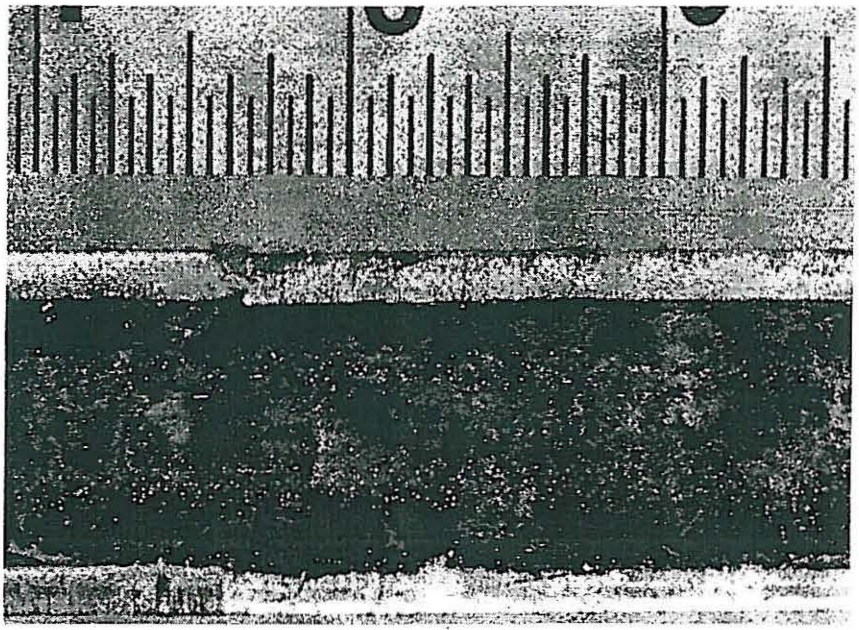


Figure 14. Iron oxide corrosion products in a building water pipe.

Figure 4-13 is an example of this effect. The deposits shown on this pipe are clearly corrosion products. However, examination of the cut edges of the pipe show that there is no significant pitting, and this was confirmed when the deposits were removed. This can have important consequences for chemical treatment. If tuberculation is severe, mechanical and/or chemical cleaning may be required so that corrosion inhibitors can reach the metal surfaces. If corrosion is not significant and the deposits are not impeding water flow or heat transfer, dispersants to gradually move the deposits may be all that is required.

### 5.5.3 Microbiologically Influenced Corrosion (MIC)

Microbiological involvement in corrosion processes has been identified on implements and structures going back as far as the Roman Empire. This was mostly a scientific curiosity until about 1980, when the commercial importance of bacteria in water side and process side corrosion problems was recognized. The term "microbiologically influenced corrosion" (MIC) was coined to describe corrosion processes in which bacteria play a significant role.

For a time, MIC became a "catch-all" phrase used to describe any process that left deposits and corrosion pits on metal surfaces. In fact, MIC has been identified as a possible contributing factor to corrosion on all common metals except titanium, and on other materials such as concrete. However, the term has been widely overused and abused, and this has led to many cases of misdiagnosis and inadequate chemical treatment of serious corrosion problems.

It is important, therefore, to keep MIC in perspective. Just as all mounds of corrosion products are not tubercles, so all tubercles do not indicate MIC.

Many tubercles form in environments in which bacteria would likely be absent. On the other hand, there are some studies which suggest that tubercular masses may be caused by iron-depositing bacteria. Bacteria are always present in open cooling water environments, and are usually found in tubercles. None of these facts indicate that bacteria are involved in the corrosion process. A simple swab test for bacteria in a deposit should never be used, by itself, as an indicator of MIC involvement.

Bacteria are clearly not the sole cause of tubercular development, nor should bacteria be considered a significant accelerant of tubercular growth a priori. It is also clearly established that bacteria do not directly attack metal surfaces. Where bacteria are involved, it is, in most cases, the acidic metabolic products of bacterial growth that accelerate corrosion.

MIC is a real phenomenon that is often a contributing factor in both tuberculation and other forms of corrosion. Figure 4-14 shows an example of MIC on a carbon steel tube sheet. A great deal of ongoing scientific research has been done in this area. Both aerobic and anaerobic bacteria can be involved, and metabolic pathways leading to corrosion of metals have been shown to be very complex.

Figure 4-14. An example of MIC on carbon steel.

From a practical point of view, and considering only tubercular corrosion of carbon steel in cooling water service, following are features that have frequently been associated with bacterial acceleration of corrosion rates beneath tubercles:

- Bacteria: Biological counts on the metal surface or in the tubercle, exceeding 100 CFU/mL for sulfate reducing bacteria (SRB) and 1,000 CFU/mL for acid producers (clostridia). These are both anaerobic strains of bacteria that grow beneath other deposits in cooling water systems.
- Deposits: Iron sulfide crystals near the corroded pit floor are usually metabolic products of sulfate reducing bacteria. Low molecular weight

organic acid salts, e.g., acetic acid, propionic acid, etc. are usually formed by acid producing bacteria.

- Morphological evidence: Deep, hemispherical, clustered pits with sharp edges superimposed upon the larger dish-shaped depressions found in tubercular corrosion seem to be common when sulfate reducing bacteria are present (see Figure 4-14). Striated pit interiors and large fluid-filled cavities may indicate acid producing bacterial activity. A filamentous structure in the tubercles can be the result of gallionella (iron depositing bacteria), but gallionella bacteria alone have not been identified as contributing directly to MIC.

### 5.5.4 Testing for MIC

Proper detection and recognition of MIC is a very important part of every corrosion study and system survey. A misdiagnosis of the nature of tubercular corrosion can lead to serious undertreatment and failure to correct the problem, or to overtreatment and unnecessary expense.

Following are field and laboratory tools that are available for detecting the presence of MIC activity in corrosion problems. Microbiological testing is discussed further in section 10.0.

- Bacterial tests: Swab tests and serial dilution field test kits are available for detecting live sulfate reducing and acid producing bacteria. Laboratory methods can detect both live and total bacteria. Dipstick tests for anaerobic bacteria are notoriously unreliable and should be avoided. Anaerobic bacteria do not live in aerated cooling tower water, so that low or zero counts tell nothing about what may be living on pipe walls (called biofilm) or beneath deposits.
- Chemical tests: Simple lead acetate test strips are a sensitive field test for sulfides in deposits and at the bottom of corrosion pits. Laboratory chemical analyses can detect all significant elements, and scanning electron microscopy can pinpoint locations of sulfur and other elements in deposits. Beware of chemical analyses for total sulfur, usually reported as sulfate. Most of this probably actually is sulfate, normally present in water and therefore trapped in small amounts in most deposits.
- Morphological examinations: Field examination of corrosion coupons with a magnifying glass or hand microscope, and laboratory metallurgical tests, can identify the morphological patterns described in section 5.5.3 as characteristic of MIC. WARNING: Morphological data alone should never be taken as confirming evidence of the presence of MIC, because these patterns are neither necessary nor unique to MIC. Morphological data plus either bacterial or chemical positive tests are a good indication, and all three together are strong evidence for the presence of MIC in a corrosion

process. See the references at the end of this chapter for good books showing photographs of various forms in which MIC can appear.

## 5.6 PITTING CORROSION

### 5.6.1 Description

Pitting is a deep, narrow corrosive attack, which often causes rapid penetration of the metal or alloy. Pitting corrosion is characterized by corrosive attack in a localized region surrounded by non-corroded surfaces, or surfaces that are attacked to a much lesser extent. Pitting corrosion can initiate in some statistical manner on an open, freely exposed surface, or at random imperfections on passive films or coated surfaces. Tuberculation, as described in section 5.5, is one form of pitting corrosion, but pits can form on metal surfaces without tuberculation or other large deposits. Figure 4-15 is one example of this type of pitting corrosion.

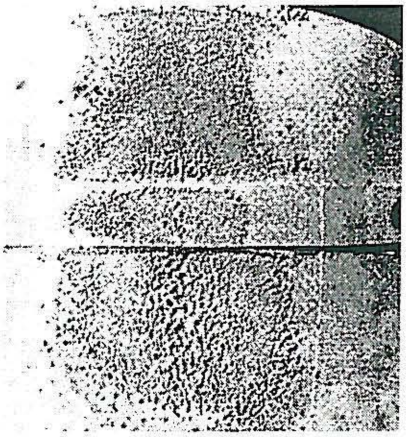


Figure 4-15. Pitting corrosion of a cast iron cylinder liner in salt water.

Often, a local corrosion cell is set up between the interior of the pit and the external surface. The interior contains acidic, hydrolyzed salts that are quite corrosive compared with the bulk solution. An anode is established within the pit, and the surrounding surfaces act as cathodes. This is particularly the case for alloys that rely on a resistant, passive film for protection such as stainless steels, nickel alloys, copper alloys, aluminum and galvanized steel (zinc). Pits develop at weak spots in the surface film and at sites where the film is damaged mechanically under conditions where self-repair will not occur. See also sections 5.4.3 and 5.5.1, above.

The practical importance of pitting corrosion depends on the thickness of the metal and on the penetration rate. The rate usually decreases with time. Thus, on thin sections, pitting may be serious, while on a thick section it may be less important. In general, the rate of penetration decreases if the number of pits increases. This is because adjacent pits have to share the available adjacent cathodic area, which controls the corrosion current that can flow. See section 5.3.4 for more on this subject.

### 5.6.2 Pitting Mechanisms

Pitting corrosion usually occurs in three stages:

- Initiation: Pits initiate at defects or imperfections in a protective or passive film. The defects may either be randomly distributed, or caused by mechanical damage to the films. In some alloys, it may take a considerable amount of time for the passive films to break down. Pitting may not initiate for long periods, but once it initiates, pitting can propagate rapidly.
- Propagation: In the propagation stage, corrosion is driven by the potential difference between the anodic area inside the pit and the surrounding cathodic area. In addition, the environment within the pit can become more aggressive and further accelerate corrosion.
- Termination: A pit may terminate because of increased internal resistance of the local cell, caused by filling with corrosion products, filming of the cathode, etc. If a pitted surface is dried out, of course the pits will terminate.

## 5.7 FLOW ASSISTED CORROSION

Flow assisted corrosion is defined as the result of the combined actions of corrosion and fluid flow or velocity. There are three well-known types of velocity-related corrosion: erosion-corrosion, impingement and cavitation. Each of these has distinguishing characteristics.

### 5.7.1 Erosion-Corrosion

Erosion-corrosion occurs when the velocity of the fluid in a piping system is sufficient to physically remove protective films from the metal surface.

- Recognition: Erosion-corrosion often causes localized attack where surface discontinuities cause flow aberrations and turbulence. This phenomenon may occur at weld beads, and in elbows and "T" fittings where sudden changes in flow direction occur. Erosion-corrosion can occur in flowing liquids or gases with or without abrasive particles.

  In this form of attack, the velocity of flow is sufficient to remove weakly adherant corrosion products from the surface as they are formed, reducing their protective effect. The flow velocity may also prevent corrosion inhibitors from forming protective films and it may also directly increase corrosion of the substrate metal. This results in an overall acceleration of the corrosion process.

- Mechanism: The fluid dynamics in erosion-corrosion by cooling waters can be an important factor in determining the rate of material removal. Turbulence is also important; that is, turbulent flow is more likely to cause erosion-corrosion than is laminar flow. A change in velocity alone can sometimes explain a sudden increase in surface damage.

When erosion-corrosion occurs, the effect of velocity on the corrosion rate usually exhibits a breakaway phenomenon. That is, a maximum velocity can be withstood without removal of the protective films. Above this limiting breakaway velocity, corrosion rates increase very rapidly. The resistance of protective films to removal plays a significant role in determining the breakaway velocity for a given alloy-environment system.

### 5.7.2 Impingement

Impingement is localized erosion-corrosion caused by turbulence or impinging flow. Entrained air bubbles tend to accelerate this action, as do suspended solids. This type of corrosion occurs in pumps, valves, and orifices, on heat exchanger tubes, and at elbows and tees in pipelines. Figure 4-16 shows an Admiralty metal condenser tube that failed due to impingement attack by entrained air.

Figure 4-16. Impingement corrosion of an Admiralty metal condenser tube.

- Mechanism: The mechanism of impingement is similar to that of erosion-corrosion, as flow removes the protective films responsible for the corrosion resistance of the material. In impingement, however, the flow is either turbulent or directed at roughly right angles to the materials, whereas, in erosion-corrosion, the flow is roughly parallel to the surface.

  When cooling water is flowing over a surface as in a pipe or heat transfer tube, there is usually a critical velocity, below which impingement does not occur and above which it increases rapidly.

- Recognition: Impingement corrosion usually produces a pattern of localized attack with directional features. The pits or grooves tend to be undercut on the side away from the source of flow, in the same way that the oncoming water undercuts a sandy riverbank at a bend in the river.

  In practice, impingement and cavitation may occur together, and the resulting damage can be the result of both. Impingement may damage protective oxide film and cause corrosion, or it may mechanically wear away the surface film to produce a deep groove.

### 5.7.3 Cavitation

Cavitation is a mechanical damage process caused by collapsing bubbles in a flowing liquid. Cavitation usually results in the formation of deep, aligned pits in areas of turbulent flow. Cavitation damage to ship propeller blades and pump impellors are well-known examples of this phenomenon. Figure 4-17 is a good example of cavitation corrosion.

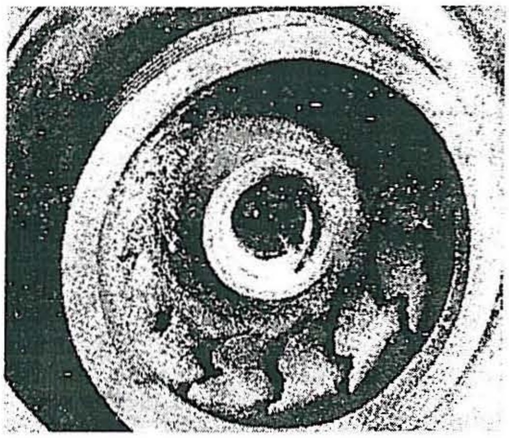


Figure 4-17. Cavitation destroyed this bronze pump impeller.

- Mechanism. Cavitation results when protective films are removed from a metal surface by the high pressures generated by the collapse of gas or vapor bubbles in a liquid. Where the energy input to produce cavitation is sufficiently high, there will be no significant contribution to the process either by hard particle impact or by corrosion. The necessary high-energy inputs can be achieved in the laboratory with suitably powered ultrasonic transducers. Under these conditions, extreme turbulence can cause the collapsing voids in the liquid to disappear in a microsecond (one millionth of a second) or so and can generate forces on the order of about 700,000 kPa (100,000 psi) as the bubbles collapse. This process can literally tear the surface apart. The action is somewhat similar to the water hammer effect in pipes when a valve is closed suddenly.
- Process. The steps through which this process is thought to occur are:
  1. Bubble formation in an area of low pressure
  2. Bubbles move to higher pressure areas
  3. Bubbles collapse, forming high-pressure waves in the liquid
  4. Pressure waves impinge on the surface, removing the protective film
  5. Corrosion may occur on the exposed metal
  6. Process repeats

## 5.8 OTHER FORMS OF CORROSION

### 5.8.1 Selective Leaching or Dealloying

Selective leaching, or dealloying, is a corrosion process in which one constituent of an alloy is removed preferentially, leaving an altered residual structure. Most engineering metals are alloys that consist of mixtures of elements. In some cases, such as zinc and copper alloyed to produce a brass, one element used is anodic with respect to the other elements in the alloy and can selectively corrode by galvanic action.

Selective leaching was first reported in 1866 on brass alloys. It has been reported since then in virtually all copper-based alloy systems, as well as in cast iron and other alloys. Dezincification of brass is still the best known example of selective leaching. Dezincification is discussed as an example at the end of this section.

- Mechanism: The dealloying mechanism can be either a selective removal of one or more alloy constituents, leaving a residual substrate, or dissolution of the entire alloy, with one or more constituents re-deposited. Laboratory investigations have shown that both processes can occur simultaneously under certain conditions. In either case, the corrosion results in a residual metal with essentially the same surface profile and volume as the parent metal. This is sometimes referred to as a "pseudomorph" of the original artifact. Typically, up to 30% or more of the original metal may corrode away, and the residual "sponge" or "plug" will have virtually no mechanical strength.

- Recognition: Dealloying is commonly detectable as a color change, or a drastic change in mechanical strength. Brasses will turn from yellow to red and cast irons, from silvery gray to dark gray. Gray iron that has suffered severe graphitic corrosion can be cut with a penknife.

  Difficulties may be encountered where deposits, colored environments, or accessibility make inspection hard. Problems will be experienced in detecting dealloying in most methods of automated inspection, because no volume change occurs and because the density difference can be masked by precipitated salts, corrosion products, etc., within the dealloyed region.

  Various laboratory techniques, such as cross-sectioning the part in question, will normally provide evidence of color changes. Metallographic examination at high magnification and x-ray spectroscopy can provide positive identification.

- Example – dezincification of brass: Dezincification of brass alloys and graphitic corrosion of cast iron are the two best-known examples of selective leaching corrosion. Yellow brass pipes, once used extensively for both industrial and municipal water piping systems, are now rarely seen in this service. Dezincification from the inside (water side) was very difficult to detect from the outside surface, so that these pipes sometimes failed without warning. Arsenical (Admiralty) brass was developed to counteract this problem. Admiralty brass is used extensively in heat exchanger tubing but not for long piping runs.

As with other alloys, dezincification of brass occurs in two modes:

1. Surface dezincification involves selective leaching of zinc from the surface of the alloy. The metal takes on the red color of copper. Surface dezincification is usually quite shallow and does not impact the mechanical strength of the alloy.
2. Plug dezincification is more serious. Deep "plugs" of zinc are selectively removed, leaving the copper structure intact. Plug dezincification occurs only on portions of the surface. The remainder is not attacked, so that depending on the configuration, the pipes or structures may retain some mechanical strength. Plug dezincification may actually penetrate pipe walls, allowing water to "weep" through the metal to the outside. Figure 4-18 shows an example of plug-type dezincification of brass.

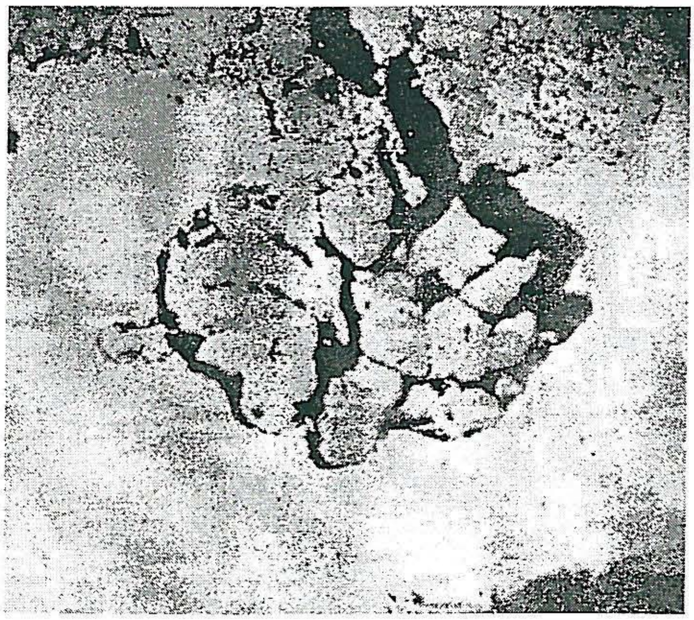


Figure 4-18. Plug-type dezincification of a brass pipe. Original magnification 25X.

### 5.8.2 Stress Corrosion Cracking

Stress corrosion cracking refers to cracking caused by the simultaneous presence of tensile stress and a specific corrosion medium.

- Definition: Stress corrosion cracking is a brittle failure mode in an otherwise ductile metal, resulting from the combined action of tensile stress and a specific corrosive environment.

  Stress corrosion cracking is not a general phenomenon. Only specific corrosive media promote stress corrosion cracking in specific alloy systems (e.g., caustic with carbon steel, chlorides with stainless steels, and ammonia with copper alloys).

- Mechanism: Stress corrosion cracking is an anodic process, a fact that is verified by the applicability of cathodic protection as an effective remedial measure. Usually there is an incubation period during which cracking originates at a microscopic level. This is followed by actual propagation. Eventually, the cracks may be self-arresting to a large extent, as in typical multibranched transcrystalline stress corrosion cracking, apparently because of localized mechanical relief of stresses.

- Recognition: Both a specific corrodant and a minimum stress level are required for stress corrosion cracking to occur. A susceptible alloy exposed in a corrosive environment, but with low or nonexistent stress, will not crack. Similarly, the same alloy, subject to high stress, but in an environment that does not contain the specific corrodant for that material, will not crack.

  The term stress corrosion cracking implies the formation of cracks. There is usually little metal loss or general corrosion associated with the corrosion process. In fact, if severe general corrosion is in progress, stress corrosion cracking usually will not occur.

- Alloys: Many environments can cause low carbon steel to fail. Among these environments are caustic, nitrates, amines, ammonia, cyanide, hydrofluoric acid, and sulfides. Cracking is mostly intergranular (along grain boundaries, section 5.8.3), and is related to the composition of the steel and whether or not the steel has been heat treated. As a general rule, low carbon steel will not stress crack in any of the named environments if it has been properly stress relieved and unusually high stresses are not imposed.

  Copper-base alloys are susceptible to a variety of environments that will cause stress corrosion cracking, including amines, nitrates, ammonia, and mercury.

  Austenitic stainless steel alloys are susceptible to stress corrosion cracking, particularly in waters containing significant levels of chloride ions. The cracking is transgranular (across grain boundaries). Figure 4-19 shows an example of stress corrosion cracking of stainless steel condenser tubes in a hot concentrated chloride environment.

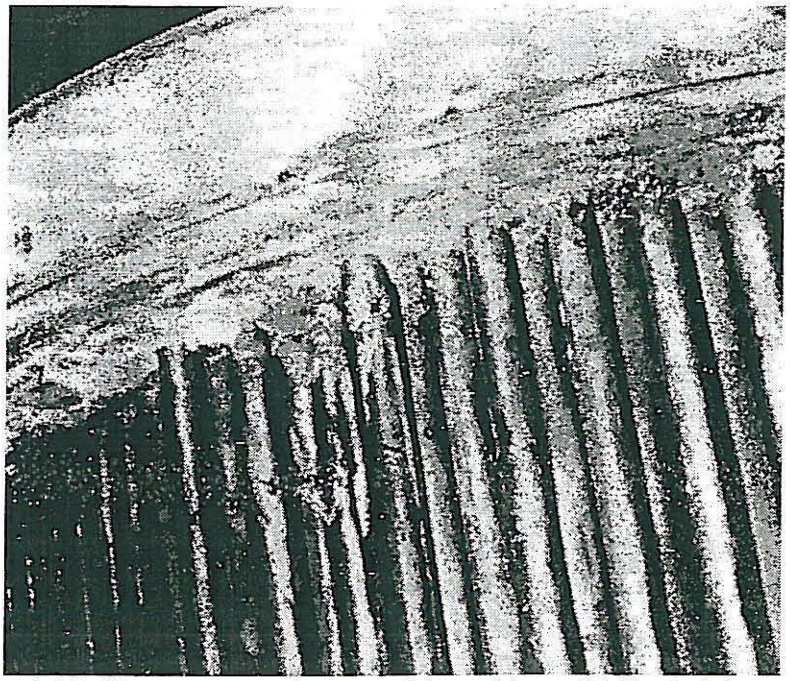


Figure 4-19. Stress corrosion cracking of type 304L stainless steel condenser tubes.

Special alloying, careful heat treatment after manufacturing and control of chloride levels are the most reliable ways to control stress corrosion cracking of stainless steels. Stress corrosion cracking of austenitic stainless steels is discussed in more detail in section 6.5.3.

### 5.8.3 Intergranular Corrosion

Intergranular corrosion refers to preferential attack at, or adjacent to, the grain boundaries of a metal.

- Recognition: As described in section 6.0, almost all engineering metals are composed of individual crystals, or grains, which meet at areas of relative impurity and misalignment called grain boundaries. Corrosion that occurs preferentially at, or adjacent to, these grain boundaries results in a very large effect compared to the actual amount of metal removed at the grain boundaries. Intergranular corrosion usually produces surfaces that are granular in appearance. In some cases, individual grains are loosened and lost from the material. In other cases, the localized loss of grain boundary material results in localized attack similar in appearance to cracking.
- Mechanism: Intergranular corrosion occurs when the grain boundaries, or the areas directly adjacent to the grain boundaries, are anodic to the surrounding grain materials. Grain boundaries may be anodic to the surrounding metal through many mechanisms. They may be anodic because of differences in impurity levels between the grains and the grain boundaries. They may be anodic because of the effective strain energy of the misalignment of atoms in the grain boundaries. The grain boundaries,

or adjacent areas, may be anodic because of the formation of precipitates due to improper heat treatment.

- Control: Intergranular corrosion appears in many common metals and alloys. Control must be based on a thorough understanding of the metallurgy, process operations and water-related operations at specific sites. There is no substitute for a thorough metallurgical examination of failed parts, and a complete survey of the system, including both process operations and water treatment. Following are some of the factors that may be involved in intergranular corrosion failures, and that can be controlled to help avoid these failures:
    - Stress. Intergranular corrosion is not necessarily stress-related. However, residual stress makes grain boundaries more anodic as explained above, and can greatly accelerate failure by encouraging cracks to widen to relieve stress as corrosion proceeds. Solution: proper annealing during manufacturing, shot-peening to relive surface stress, and careful construction to avoid applying unusual stress.
    - Environment. Intergranular corrosion is a galvanic problem as explained above, but this does not mean that galvanic corrosion between the grain boundary material and the surrounding metal will necessarily occur. The environment must be corrosive and must support the specific corrosion reactions involved. Many corrosion reactions are self-limiting because the corrosion products stifle the reaction (polarize the surface, see chapter 1 and section 5.9). Thus, aluminum, zinc, chromium and other metals form oxide coatings that protective the metal surfaces. In neutral and mildly alkaline environments, from about pH 7 to 8.5, where these oxides are stable, little or no corrosion will occur. However, if the pH is allowed to become acid or strongly alkaline, the oxide coatings may dissolve, allowing intergranular attack to proceed.
    - Water treatment. With the environment under control as above, the zinc, phosphate and molybdate-based corrosion inhibitors commonly used in cooling water systems (section 5.10) can further protect metal surfaces and help to control intergranular corrosion.

### 5.8.4 Hydrogen Induced Cracking

Hydrogen induced cracking of steel alloys is not normally encountered in cooling water systems. It is sometimes a problem in high-pressure boilers, and it is a serious potential problem in many process water systems. Therefore it deserves mention in this manual.

This form of cracking occurs mostly in acidic water environments. The corrodant may be hydrogen sulfide gas in solution, carbon dioxide, chlorides or other acidic compounds. Cracking occurs in three stages:

1. Hydrogen atoms adsorb on the metal surface as a result of the cathodic corrosion reaction in acid solutions (chapter 1).
2. Adsorbed hydrogen atoms diffuse into the metal surface (actually become soluble in the metal).
3. Hydrogen atoms in the metal collect at grain boundaries and at voids around foreign inclusions in the metal, called hydrogen traps. The atoms come out of solution and combine to form hydrogen molecules. The gas develops very high pressure inside these voids, causing crack initiation and propagation. The result may be blistering of the metal surface and/or loss of mechanical strength, sometimes leading to catastrophic failure.

## 5.9 POLARIZATION AND PASSIVATION

### 5.9.1 Corrosion Mechanism Review

Chapter 1, section 8 of this manual should be reviewed as background for understanding the mechanisms of corrosion inhibition discussed in this section.

As a brief review, corrosion reactions of metals in water are electrochemical in nature. They consist of two separate reactions:

- An anodic reaction, in which metal is dissolved to produce metal ions in solution and corrosion products, either on the metal surface or dispersed in the water; and
- A cathodic reaction in which dissolved oxygen is reduced to form hydroxide ions, or in acid solutions hydrogen ions are reduced to hydrogen gas.

Thus, when steel (iron) corrodes in water, the anodic reactions are:

$$2Fe^0 = 2Fe^{+2} + 4e^- \qquad (4\text{-}22)$$
$$2Fe^{+2} + 4OH^- = 2Fe(OH)_2\downarrow \qquad (4\text{-}23)$$
$$4Fe(OH)_2 + O_2 + 2H_2O = 4Fe(OH)_3\downarrow \qquad (4\text{-}24)$$

The corresponding cathodic reaction is the reduction of oxygen,

$$O_2 + 2H_2O + 4e^- = 4OH^- \qquad (4\text{-}25)$$

or in acid solution, the reduction of hydrogen ions:

$$2H^+ + 2e^- = H_2\uparrow \qquad (4\text{-}26)$$

These reactions involve a transfer of electrons. This means that an electric current, called the corrosion current, must flow from anodes to cathodes through the metal surface, and back to the anodes through ions in the water, as shown in figure 1-12 in chapter 1.

### 5.9.2 Polarization

Any process that interferes with either the anodic or the cathodic reaction, or with both reactions, will reduce or stop the flow of current and hence reduce or stop corrosion. Two naturally occurring processes that limit the flow of corrosion current are called polarization and passivation.

Most corrosion reactions in water systems are self-limiting. The products of the anodic and cathodic reactions – ferrous and ferric hydroxides at the anodes, and hydroxides and calcium carbonate at the cathodes – tend to shield the metal surface and prevent ready access of water containing dissolved oxygen. This process, called polarization, limits the rate of the cathodic reaction and hence reduces the corrosion rate.

For this reason, initial high corrosion rates tend to slow down and approach a limiting value that depends upon the configuration of the surface and the composition of the water. High flow velocities and/or high turbulence can overcome this polarization effect. Corrosion rates then increase because corrosion products cannot accumulate to help shield the metal surface.

### 5.9.3 Passivation

As explained in chapter 1, elements that are high in the galvanic series (Table 4-1) are so reactive that they cannot exist as the free elements under atmospheric conditions. Sodium and potassium, for example, react violently with water. These are, in effect, simply extremely rapid corrosion reactions.

However, other elements close to the top of Table 4-1, such as magnesium, aluminum and zinc, that are also very reactive as free elements, are stable in contact with air and water, and are widely used as materials of construction. The difference is that these elements form stable oxide films that effectively seal the surface and prevent all contact with water and air. This process is called passivation. The dull gray film seen on galvanized steel that has been exposed to air is a good example of a naturally formed passive film. Stainless steels earn that title by forming a very thin, mostly invisible film of chromic oxide on the surface that prevents corrosion.

An important property of naturally formed passive films is that they are self-repairing. If the film is damaged, a small amount of corrosion occurs to reform the film, and the surface again becomes passive. This is true as long as the environment does not attack the oxide film. Thus, galvanized steel is commonly used for cooling tower construction. However, the pH of the water must not be allowed to range below about 6.5 or above about 8.5. Outside of this range, the oxide film dissolves and the zinc coating corrodes away. Similarly, stainless steels are stable in sulfuric acid, which provides an oxidizing atmosphere, but they corrode readily in hydrochloric acid, a reducing acid.

The terms passivation and passive films refer to protective films formed by direct reaction of a metal with its environment, without any external additives. However, these terms are also used to describe protective films formed by corrosion inhibitors (section 5.10) and by oxygen scavengers (chapter 3).

## 5.10 CORROSION INHIBITORS

### 5.10.1 Types of Inhibitors

Corrosion inhibitors are simple inorganic or organic chemicals that, when added to water at mg/L dosage levels, interfere with the electrochemical corrosion reactions on steel, copper and other metals, and dramatically reduce corrosion rates.

Specific corrosion inhibitors are discussed in the following sections. Corrosion inhibitors as a group fall into three general classifications:

- Reactive inhibitors chemically react with (corrode) the metal surface to produce a protective film (sometimes called a passive film) that is chemically bonded to the surface and contains both oxidized metal and some form of the inhibitor. These films are quite stable. They are resistant to velocity and turbulence effects and usually provide some residual corrosion protection for a time if inhibitor feed is discontinued for any reason. Chromate and nitrite on steel, and various azoles on copper, are typical examples of reactive corrosion inhibitors.
- Precipitating inhibitors provide corrosion protection by precipitating an inert barrier layer on the metal surface. These layers are not chemically bonded to the surface, but when well formed, they can be quite resistant to flow velocity and turbulence. Zinc, forming zinc hydroxide films, and phosphate, forming ferric and calcium phosphates, are typical examples of precipitating inhibitors.
- Filming inhibitors are chemicals, such as amines, organic acids and other polar organic molecules that form chemical or electrostatic bonds with the metal surface, without actually corroding the surface. Many of these molecules contain a charged ionic group at one end that attaches to the surface, and a hydrophobic group that extends outwards and helps to keep water away from the surface. Filming inhibitors are very useful, but they are the least stable to flow velocity and turbulence. Filming amines used in boiler condensate corrosion control are examples of filming inhibitors.

Corrosion inhibitors are also classified in terms of the corrosion reaction that they inhibit:

- Cathodic inhibitors interfere with the cathodic reaction, reduction of oxygen (equation 4-25). As explained in chapter 1, corrosion reactions in cooling water environments are under cathodic control. That is, the rate of the cathodic reaction, governed by the rate at which dissolved oxygen can diffuse to the metal surface, controls the overall corrosion rate. By reducing the available cathodic area, cathodic inhibitors proportionally reduce the overall corrosion rate.

- Anodic inhibitors suppress the anodic reaction, that is, metal ions going into solution (equation 4-22). Anodic inhibitors are very effective in controlling general corrosion, because they directly protect the corroding sites. However, anodic inhibitors can also stimulate pitting attack if maintained below a critical concentration. Since the overall corrosion reaction is under cathodic control, reducing the available anodic area does not directly reduce the corrosion rate; it simply concentrates the attack on any available anodic sites. As explained more fully in chapter 1, this can lead to serious localized pitting corrosion. For this reason, anodic inhibitors are also called "dangerous inhibitors". Minimum concentrations of anodic inhibitors required for good protection have been determined experimentally for each product. These concentrations will vary somewhat with water quality. High dissolved solids and low alkalinity waters will require higher inhibitor dosages for safe protection.
- Mixed inhibitors are blended products that suppress both the anodic and cathodic reactions. This is a desirable way to gain the benefit of the good protection of anodic inhibitors with added safety from the overall reduction in corrosion rate from cathodic inhibitors. Many commercial corrosion inhibitors are formulated in this way.
- General inhibitors, or filming inhibitors as above, cover the entire surface of the corroding metal through the development of adsorbed protective films. Sometimes these films are polymeric in nature.

### 5.10.2 Inhibitor Selection

Many different corrosion inhibitors, alone and in various combinations, are available to provide protection to the engineering alloys used in cooling water treatment. However, selecting the proper inhibitor is not always a simple matter. A good understanding of the system, including water chemistry, operating routines, system metallurgy and critical heat exchangers, is required, along with good product line knowledge. See the discussion of system surveys at the end of this chapter, for more on this important subject.

Following are some general criteria for corrosion inhibitor selection:

- The inhibitor must protect all exposed metal from corrosive attack.
- The inhibitor must be effective at low, cost-effective dosage levels, and at reasonable cycles of concentration and pH, in the site-specific water.
- The inhibitor should be effective under a broad range of operating conditions, i.e. temperature, pressure, flow rate, process demands and timing, etc. to allow for system variability.

- The inhibitor must not form deposits other than inhibiting films on the metal surface.
- The inhibitor should not stimulate microbiological activity, or the microbiological treatment program must be designed to control this problem.
- The inhibitor should have minimal toxicological effects when discharged, and it should be acceptable in the receiving waterway or sewer. In some cases, specific treatment of the blowdown water may be required.

Many different corrosion inhibiting chemicals can be used alone, or in various synergistic combinations, to provide multimetal protection in cooling water systems. Following are brief descriptions of the most widely used cooling water corrosion inhibitors.

### 5.10.3 Chromate

Chromate is included in this manual because of its historical significance. Before about 1985, chromate was used extensively as a corrosion inhibitor. It is a reactive, anodic inhibitor, extremely effective over a wide range of operating conditions, especially in open cooling tower systems when blended with cathodic inhibitors such as zinc or polyphosphate.

However, in the late 1980s, chromate was banned because of its toxicological impact on the environment (chromate is a known carcinogen). With chromate no longer available for open system use, other inhibitors had to be developed to provide needed corrosion protection. Newer products are more environmentally friendly, and can be equally effective.

Some tightly regulated closed systems still use chromate-treated water, particularly in severe service applications and where the water is very corrosive. In such cases, operating personnel are required to maintain control of the entire inventory of treated water, and to report any losses or discharge to both state and federal environmental authorities.

### 5.10.4 Orthophosphate

Phosphate-based chemicals are the most widely used corrosion inhibitors in open cooling water systems. Trisodium orthophosphate, $Na_3(PO_4)_2$, is simply the trisodium salt of orthophosphoric acid, $H_3PO_4$. The disodium and monosodium salts are also available. These are widely used for pH and alkalinity control in boiler water treatment as well as in open cooling water systems (see chapter 3).

The orthophosphate anion is the simplest species in this family of corrosion inhibitors. It is an anodic, precipitating inhibitor, that effectively inhibits corrosion of low carbon steel by precipitating ferric phosphate, $FePO_4$, at anodic sites. Good corrosion control can be achieved above pH 7.5, especially in soft water systems. Below this pH, orthophosphate is less effective because ferric phosphate becomes soluble. Phosphate chemistry is sensitive to water quality, especially chloride content. High concentrations of chloride (above 300 mg/L) reduce the efficiency of orthophosphate-based corrosion inhibitors by promoting localized pitting attack.

When orthophosphate can be used, protective film formation is very rapid and tenacious. Orthophosphate works synergistically with other inhibitors to provide excellent corrosion protection, similar to chromate. A major concern with orthophosphate is the potential for calcium phosphate precipitation in high pH and hard waters (see chapter 1).

It is often suggested that orthophosphate should also act as a cathodic corrosion inhibitor, because tricalcium phosphate, $Ca_3(PO_4)_2$, becomes very insoluble at the higher pH levels generated at cathodic sites (chapter 1). In fact, this is probably correct. However, tricalcium phosphate precipitates slowly, as the end product of a chain of complex intermediate phosphates, while ferric phosphate precipitates quickly at the anodic sites. Therefore, in a corroding system, any cathodic inhibition achieved by orthophosphate is overshadowed by the immediate anodic protection provided by ferric phosphate. In a well-protected system, where little or no corrosion takes place, tricalcium phosphate, if it is allowed to form, will provide additional cathodic corrosion protection over time.

Many large municipalities add roughly 1 mg/L of orthophosphate to their water supplies, in order to precipitate small amounts of lead dissolved from old piping systems. It is important to consider this in planning a chemical treatment program. When concentrated in a cooling tower, makeup water phosphate can be a significant factor in both corrosion control and potential precipitation of calcium phosphate scale.

### 5.10.5 Polyphosphates

Phosphate chemistry is a complex subject that is beyond the scope of this manual. Briefly, phosphates can polymerize, just like many organic molecules, to form several different classes of polyphosphate compounds. The compounds most often used in cooling water treatment include:

- The dimer, tetrapotassium pyrophosphate.
- The trimer, sodium tripolyphosphate.
- Sodium hexametaphosphate.

Polyphosphates are classified as cathodic precipitating inhibitors. They react with calcium under high pH conditions at cathodic sites (chapter 1) to form a thin, protective film of calcium polyphosphate. Polyphosphates provide corrosion protection for carbon steel in an effective pH range from 6.5 to about 8.0. A minimum of about 50 mg/L calcium hardness is essential if polyphosphates are to function as corrosion inhibitors. Other than hardness, polyphosphates are relatively insensitive to water quality. Sometimes, polyphosphates are combined with zinc, another cathodic corrosion inhibitor, to improve performance (zinc polyphosphate and zinc hydroxide are both insoluble in the normal open cooling water system pH range.

A concern with polyphosphates is that they revert (depolymerize) to form orthophosphate and increase the potential for calcium phosphate precipitation. Reversion rates are increased by low pH and high temperature. Pyrophosphate is the most stable of the common polyphosphates, while tripolyphosphate is the least stable. Conveniently, the potassium salt, tetrapotassium pyrophosphate, $K_4P_2O_7$, is very soluble, so that liquid formulations containing pyrophosphate as a corrosion inhibitor can easily be made.

Because of their ability to form soluble complex ions with calcium, polyphosphates are sometimes used as chemical softening agents in domestic water supplies.

### 5.10.6 Phosphonates

Organic phosphate compounds are called phosphonates. Phosphonates are distinguished from inorganic polyphosphates in that all phosphonates contain direct carbon-phosphorus bonds. Phosphonates are primarily used in cooling water treatment to control calcium carbonate scale (section 6.0), but they also have corrosion-inhibiting properties.

Phosphonates belong to the class of compounds known as general precipitating inhibitors that protect both anodic and cathodic sites. The compounds that precipitate to form protective films are calcium and iron salts. The composition of the film depends upon the phosphonate, the specific blended formulation in use, the composition of the circulating water and operating conditions.

A problem with all phosphonates is that like polyphosphates, they decompose over time to form orthophosphate. As a group, phosphonates are more stable than inorganic polyphosphates, but decomposition rates increase with temperature and with low pH. Phosphonates are also attacked by oxidizing biocides (chlorine and bromine compounds). All of these factors must be considered when designing chemical treatment programs including phosphonates.

- HEDP (1-hydroxethylidene 1,1 diphosphonic acid), when used alone, is a relative poor corrosion inhibitor. However, when formulated with zinc, it provides good protection. The effective pH range is 7 to 9. HEDP requires at least 25 to 50 mg/L calcium (as carbonate) in the water for film formation. However, at calcium levels above about 300 mg/L as calcium carbonate, HEDP can precipitate as a calcium-HEDP salt. This can lead to loss of both mineral scale and corrosion control, and to formation of calcium-HEDP scale. Polymers can be added to the formulation to help prevent precipitation of the calcium phosphonate salt. HEDP is more resistant to attack by chlorine than is AMP (below), but not as resistant as PBTC.

- AMP [aminotri(methylenephosphonic) acid] also is a relative poor corrosion inhibitor when used alone. In the presence of zinc, excellent corrosion protection on carbon steel can be achieved, especially in soft water. AMP contains a nitrogen atom to which three methlyene phosphonate groups are bonded. These nitrogen bonds weaken resistance to chlorine, so that AMP is rapidly degraded. The effective pH range is 7 to 9. AMP is more tolerant of high calcium levels than is HEDP, but in high hardness water, AMP can form a complex and precipitate a calcium-AMP salt that can add to system scale.
- PBTC (2-phosphonobutane, 1,2,4-tricarboxylic acid) is one of the most stable of the phosphonates. It will not degrade in the presence of typical chlorine levels in cooling water systems. When used with zinc, PBTC can provide excellent carbon steel corrosion protection. It also has good tolerance towards calcium, so that calcium phosphonate precipitation is not a potential problem.
- HPA (hydroxyphosphonic acid) is a phosphonate that was specifically designed for carbon steel corrosion protection, rather than calcium carbonate scale control. When used alone, HPA requires calcium in the water for effective protection of carbon steel. However, in combination with zinc, HPA provides excellent corrosion control on carbon steel in soft water. HPA degrades easily with low levels of chlorine in water, but the manufacturer claims that this reaction can be controlled by adding monoethanolamine (MEA) to the formulation.
- Bricorr 288C, (a phosphonocarboxylic acid) provides corrosion protection similar to HPA, but with much improved resistance to chlorine oxidation.

All of the above phosphonates are chelants and will complex with zinc, which helps in providing good corrosion control to carbon steel. However, due to their chelant nature, phosphonates can attack copper. To avoid this problem, specific copper corrosion inhibitors should always be included when phosphonates are used in systems containing copper components.

### 5.10.7 Molybdate

The chemical structure of the molybdate ion ($MoO_4^{-2}$) is similar to that of chromate ($CrO_4^{-2}$), and molybdenum and chromium are in the same group in the periodic table of elements (Table 1-1). Some of the chemical properties of the molybdate and chromate ions are similar. Since molybdates have low toxicity, it was thought that molybdate would make an ideal replacement for chromate as a corrosion inhibitor. However, experience has shown that this is not the case.

Molybdate is an anodic precipitating inhibitor, while chromate is anodic and reactive. Molybdate and chromate are both oxidizing agents, but chromate is much more powerful, especially under alkaline cooling water conditions. Chromate forms bonded protective films on carbon steel, while at low dosages, molybdate films are simply precipitated ferric molybdate. Molybdate does become a reactive inhibitor on carbon steel in open systems, but only at high concentrations when used alone (minimum 100 mg/L as Mo, compared to 20-25 mg/L for chromate). Molybdate compounds are also substantially more expensive than chromates. The effective pH range for molybdate used alone is 6.5 to 8.5.

For these reasons, molybdate is rarely used alone as a corrosion inhibitor in open cooling systems. However, when properly formulated with other corrosion inhibitors, molybdate can be very beneficial in open recirculating cooling systems:

- In combination with ortho or polyphosphates, or zinc, as little as 3-5 mg/L molybdate as Mo can help to prevent pitting and under-deposit corrosion in low hardness systems. This is one of the strengths of molybdate formulations.
- At levels of 6-12 mg/L as Mo, formulations with phosphonates, phosphates or zinc can provide excellent protection against both general and localized corrosion in circulating waters over a wide range of hardness and conductivity. The effective pH range for formulated molybdate-based corrosion inhibitors can extend up to 9.0.
- At very high molybdate dosages, calcium molybdate can precipitate in moderate-to-high hardness waters. This problem is rarely seen.

In tight closed systems, where one fill of chemicals can last a long time, molybdate alone can be used cost-effectively. Dosages up to 500 mg/L as Mo provide excellent corrosion protection on steel.. This allows molybdate to be used in closed systems that are subject to microbiological degradation of nitrite (see below). Alternatively, the molybdate level in closed system products can be reduced to about 75 mg/L as Mo by formulating with nitrite at 350 to 500 mg/L as nitrite ($NO_2^-$).

### 5.10.8 Silicate

Silicates are used as corrosion inhibitors for steel and copper alloys in soft potable water systems where no heat transfer is involved and dissolved solids levels are low. The effective pH range is above 7.0. The protective film develops slowly over time, usually in a matter of weeks. In most open recirculating cooling water systems, this is not acceptable. Because of the higher dissolved solids content of concentrated cooling water, corrosion rates are higher. Sufficient corrosion often occurs in a short time to coat the metal surfaces with corrosion products and thus prevent any effective silicate scale from forming. For comparison, phosphate-based corrosion control programs may develop a protective film within a few hours. For these reasons, silicate is not a common chemical treatment for open recirculating cooling water systems.

Silicates can be useful corrosion inhibitors in closed systems, that are usually clean so that silicate films can form. Dosages of 50 to 100 mg/L as $SiO_2$ are required. In closed systems, silicates can be used at lower dosages (10-25 mg/L) to provide corrosion protection for aluminum and copper alloys. In such systems, silicates are blended with nitrite or molybdate in balanced formulations.

### 5.10.9 Zinc

Zinc is a mediocre corrosion inhibitor for carbon steel when used alone. However, it is a valuable synergistic addition to almost all other corrosion inhibitors in open cooling water systems, providing an added level of cathodic, precipitation-type protection to reduce the overall corrosion rate. The precipitated film is zinc hydroxide or a complex zinc hydroxycarbonate, depending upon the circulating water composition and temperature. These films form preferentially at cathodic sites because of local high pH conditions (chapter 1).

Some of the benefits of adding zinc to any corrosion inhibitor formulation are :

- Improved protection.
- More tenacious films.
- Faster film formation.
- Lower required concentrations of other inhibitors, compared to use without zinc.

Zinc therefore is always used in formulations with other corrosion inhibitors. The effective maximum pH for zinc-containing systems without stabilization is 7.5 Above pH 7.5, zinc hydroxide precipitates in the bulk water, so that corrosion protection is lost.

However, this problem is easily solved by incorporating zinc-stabilizing polymers in the formulation. These polymers help to prevent zinc hydroxide from precipitating in the bulk water, but allow it to form under the higher pH conditions that exist at cathodic sites. With polymers present, zinc-containing corrosion inhibitors can be used up to about pH 8.5. Effective zinc levels are between 0.5 and 5.0 mg/L as Zn. Proper selection and dosage of the stabilizing polymer is critical for the success of these programs. Zinc is rarely used in closed systems.

### 5.10.10 Nitrite

In the United States, the use of nitrite as a corrosion inhibitor for carbon steel is confined primarily to closed cooling water systems and hot water heating boilers (chapter 3). Usually programs containing nitrite are formulated with a high pH buffer (borax) to control the cooling water pH at approximately 9.0 to 10.0. pH 9.0 to 9.5 is the range for minimum corrosion of copper.

Nitrite, like chromate, is a true anodic reactive corrosion inhibitor. It directly reacts with (corrodes) steel, without requiring any dissolved oxygen, to form a protective oxide film, usually magnetite ($Fe_3O_4$). Thus, nitrite is a true passivating agent, because it encourages formation of a passive film on steel without itself being involved in the film.

The effective nitrite concentration, when used as the only corrosion inhibitor in closed systems, should be between 500 and 1,000 mg/L as $NO_2^-$. This concentration is required to counter the corrosive effects of dissolved solids, especially chloride and sulfate anions, and to provide some reserve protection. However, nitrite concentrations as low as 250 mg/L have been successfully applied. The nitrite level in hot water systems should be between 1,000 and 1,500 mg/L as $NO_2^-$ to provide sufficient reserve protection, but again, lower levels have been successfully applied. See chapter 3 for more on the use of nitrite in hot water boilers.

Nitrite programs in closed systems require an azole (see below) to provide protection to copper and copper alloys. Other constituents are added to the treatment program for protection of other alloys. Nitrate ($NO_3^-$) is added to protect aluminum. Silicates can also provide protection to both copper and aluminum alloys.

Nitrite is compatible with glycol-based (freeze-protected) closed systems. It is also less toxic than chromate. However, nitrite will abrade mechanical pump seals at concentrations above about 4000 mg/L.

Nitrite is often blended with molybdate in closed system programs, to reduce the total amount of chemical required, and therefore the program cost. For example, a system that can be treated with either 500 mg/L molybdate as Mo or 1,000 mg/L nitrite as $NO_2^-$, can be treated equally well with a combined program containing 75 mg/L molybdate and 300 mg/L nitrite.

A serious problem associated with nitrite in closed systems is degradation by bacteria. Nitrifying bacteria will oxidize nitrite to nitrate, while denitrifying bacteria will reduce nitrite to either nitrogen gas or ammonia. In either case, corrosion protection on steel is lost. Ammonia is aggressive to copper base alloys and can cause stress corrosion cracking in brass. Nitrite-based closed systems should be tested monthly for anaerobic bacteria. A long-lasting anaerobic microbiocide such as glutaraldehyde is often added to these systems for protection against microbiological contamination (see section 9.0).

### 5.10.11 Copper Corrosion Inhibitors

A group of organic nitrogen-containing chemicals called azoles are effective corrosion inhibitors for copper and copper alloys in both open and closed cooling water systems. The two most widely-used compounds from this group are benzotriazole and tolyltriazole. Both materials provide excellent protection to copper-base alloys. Tolyltriazole is less expensive, but benzotriazole is more easily formulated.

Azoles are general, reactive corrosion inhibitors for copper alloys. They function by forming a self-limiting reacted film over the entire copper surface. The film contains both copper and azole. The film forms rapidly and is very stable and tenacious.

In open cooling water systems, azoles should always be part of the chemical treatment program whenever the system contains copper piping or tubing, or brass or bronze component equipment. The dosage of tolyltriazole or benzotriazole should be at least 2-4 mg/L active (free) azole. Lower dosages are sometimes used for cost-control reasons, but this has been shown many times to be risky.

In chlorinated cooling systems, the active azole level should be at least 3 mg/L to provide adequate protection. Chlorine or hypochlorite at 0.5 mg/L free available halogen (FAH) applied continuously attacks both tolyltriazole and benzotriazole. There is some evidence that chlorinated azoles are still active corrosion inhibitors for copper, but the films are less stable and protective. At higher chlorine levels (above about 1 mg/L), chlorine destroys the benzotriazole and tolyltriazole molecules, so that all corrosion protection is lost.

Azoles are equally important parts of closed cooling system programs when the system contains copper evaporator tubes, air handlers or fan coils, or copper piping. Closed system dosages should be at least 10 mg/L, and preferably 25 to 50 mg/L active benzotriazole or tolyltriazole.

### 5.10.12 Vapor Phase Corrosion Inhibitors (VCI)

Vapor phase corrosion inhibitors, or volatile corrosion inhibitors (VCIs), are similar to organic filming inhibitors, as explained above. They form protective films on metal surfaces without regard to anodic and cathodic areas. VCIs possess moderately high vapor pressures plus some water solubility. They have the unique ability to inhibit atmospheric corrosion of metals without being applied directly on the metal surface.

Vapor phase corrosion inhibitors are different from volatile compounds such as amines used as corrosion inhibitors in boiler steam line treatment (chapter 3, section 7.7.) Amines require steam for transport through the condensate system, whereas vapor phase inhibitors volatilize by themselves and diffuse throughout the system.

Vapor phase corrosion inhibitors have been used for years to prevent corrosion in enclosed spaces, such as sealed packages and the interior of machinery during shipment. An advantage of VCIs is that the volatilized molecules can protect hard-to-reach spaces such as in electrical and electronic enclosures, between two metal flanges, void spaces, and similar systems.

VCIs are also an important tool for protecting cooling water, boiler water and fire protection systems from corrosion under stagnant or layup conditions. They protect the liquid phase, the vapor space and the liquid/vapor interface, which is often a source of severe localized corrosion. VCIs are supplied as pumpable liquids, and also as liquids or solids in water-soluble bags that can be placed inside the equipment to be protected. They are environmentally benign and present no disposal or equipment startup problems.

Applications of VCIs in cooling water and fire protection systems are discussed in sections 10.5.3 and 10.5.4, and boiler water applications are discussed in chapter 3, section 10.2.3.

# 6.0 Behavior of Metals in Cooling Water Systems

## 6.1 INTRODUCTION

To fully understand many of the mechanisms of corrosion as they occur on engineering materials, it is necessary to understand the fundamentals of the structure and properties of materials.

Metals are very widely used because of their combination of strength, ductility, toughness, formability, and (if properly matched to their environment) resistance to corrosion. A metal is distinguished from a nonmetal by its luster, malleability, good electrical conductivity, good thermal conductivity, and unfortunately, its ability to give up electrons, or corrode.

### 6.1.1 Metallurgy Concepts

Most of the metals used in engineering and construction are alloys, and almost all are aggregates of numerous small crystals.

Alloys are mixtures of two or more elements. The basic characteristics of an alloy come from the elements that are used. By manipulating the distribution of the elements within the crystals and the size and shape of the crystals, alloys with a wide variety of properties can be produced. The distribution of the elements within the alloy and the crystalline structure may both be controlled through thermal and mechanical treatments.

The crystalline structure of a metal is not obvious in most cases. In most metals the crystals, sometimes called grains, are very small and conform to the surface of the metal. In a typical metal, these grains range from 0.25 mm to 0.025 mm (0.01 inch to 0.001 inch) in size. The atoms in the metal grains are arranged in a regular three-dimensional pattern. This pattern, or crystal structure, is made up of repeating patterns of atoms called unit cells. In most metals, these unit cells are of three types:

- Body-centered cubic.
- Face-centered cubic.
- Hexagonal close-packed.

Within each grain, the crystal structure is normally fairly uniform. The grains are initially formed as the metal solidifies from the molten state. Each crystal starts to grow from an initial point, called a nucleation site. The crystals grow from the molten metal in a uniform pattern until they finally meet and the metal totally solidifies. Having started from many sites, the crystal structures are not aligned with each other. They meet at areas of disorder called grain boundaries, that form a three-dimensional network. The material enclosed within the grain boundaries are called grains. The grain boundaries tend to be less pure than the crystal grains themselves, as impurities that are rejected as the metal atoms form their regular crystal structure accumulate at the grain boundaries.

The crystal structure within the metal grains is not perfect. Imperfections can arise from the presence of atoms of different sizes in the crystal structure or from atoms missing from unit cells. Atoms of different sizes may either be impurities or intentionally added alloying elements. Imperfections can also arise simply from misalignment of atoms within the crystal or from extra atoms that are trapped between atoms in unit cells.

### 6.1.2 Alloying

By mixing different metals together, and sometimes by adding nonmetals such as carbon, engineering metals with a wide variety of mechanical and corrosion-resistance properties can be manufactured. Alloys are usually made during the melting process, but alloys can also be made through high-energy milling of powders with subsequent high-pressure pressing and heating without melting.

Alloys are of two basic types, solid solution and multiphase.

- Solid-solution alloys, such as brass, are made by mixing two or more metals, dissolved in each other, in a molten state. As they solidify, the atoms occupy random locations in the crystal structure, and the resulting structure is uniform and homogeneous. The properties of these solid-solution alloys are usually somewhere between the properties of the metals that are used to make the alloys.
- Multiphase alloys: In other cases, the metals dissolve in one another at high temperatures but, as they cool, separate into discrete crystals with different chemical compositions and crystal structures. These crystals, each with its own composition and structure, are called phases and can have very different properties from each other. These phases commonly form at temperatures below the melting point of the alloy through solid-phase reactions.

  The properties of multiphase alloys are dependent on the amount, size, shape, and distribution of these phases. Properties can be manipulated by heat treatment, mechanical working, or both. Manipulation of these phases can produce a wide variety of mechanical and corrosion-resistance properties in a metal with a single composition.

The basic metallurgical structure of metals and alloys affects not only their mechanical and physical properties, but also their resistance to corrosion.

Alloys should be specified by the Unified Numbering System (UNS). The UNS is not a specification but an identifier of the alloy for which controlling limits have been established in specifications published elsewhere. Once a UNS is specified, any manufacturer can produce the alloy. The alloy will have the same nominal chemical composition, independent of supplier. Some alloys are listed as trade names by different manufactures. Use of the UNS system eliminates this confusion.

## 6.2 CARBON AND LOW-ALLOY STEELS

Carbon and low-alloy steels are by far the most commonly used engineering metals. They are relatively inexpensive, readily available in a large number of shapes and sizes, and have a wide range of mechanical properties. They can be heat-treated to give the best combination of strength and ductility for specific applications. They are readily weldable both in the shop and in the field. The most commonly used steels are the carbon steels that are essentially iron-carbon alloys.

The most common carbon steels contain about 0.2% carbon, although the carbon content of carbon steels overall can vary widely. The corrosion resistance of all the carbon steels is about the same in exposure to most environments, but may vary slightly with carbon content in some chemical environments, such as strong sulfuric acid.

Low-alloy steels are carbon steels with varying small amounts of such elements as chromium, nickel, copper, molybdenum, phosphorous, and vanadium added. The total alloy addition content can be up to a few percent. These alloy additions primarily enhance the steels' mechanical properties, but some of the low alloy steels have substantially better corrosion resistance in atmospheric environments than ordinary carbon steel or other low-alloy steels.

Table 4-2 lists the UNS data for carbon steel and some low alloy steels.

**Table 4-2**

**UNS for Carbon and Low Alloy Steels**

| Alloy | UNS |
|---|---|
| SAE/AISI 1020 | G10200 |
| Ni-Cr steel (0.30%C) | G31300 |
| Cr-Ni-Mo Steel | G43xx0 |
| Cr-V Steel | G61xx0 |

The 'xx' values in Table 4-2 specify the carbon content of each alloy.

Carbon and low alloy steels are used as components in heat exchangers, HVAC chillers, boiler systems, distribution piping, valves and fitting pumps, and tanks.

Some of the more common forms of corrosion that occur on carbon steel are: uniform corrosion, tuberculation, microbiologically influenced corrosion (MIC), galvanic corrosion and caustic stress corrosion cracking. Forms of corrosion are explained in section 5.0.

Both low carbon and low alloy steels are subject to erosion corrosion and are prone to impingement and cavitation damage.

## 6.3 CAST IRON

Cast irons contain much larger amounts of carbon than carbon or low-alloy steels, usually in the range of 2% to 4%. Cast iron is low cost and can be formed into a wide variety of shapes ready or nearly ready for final use.

Most cast irons contain free carbon in the form of graphite. The shape and amount of the graphite phase has a great effect on the mechanical properties of cast iron, particularly with respect to ductility.

- Gray cast irons contain carbon in the form of flakes, and are relatively brittle alloys.
- Malleable cast irons contain graphite in the form of rosettes or clusters, and are much more ductile than gray cast irons.
- White cast irons are hard and brittle, and have much of their carbon in the form of iron carbide instead of graphite. Formation of graphite in white cast irons is inhibited by the low silicon content of these alloys, and by fast cooling of the castings.
- Ductile cast irons have their graphite in the form of nodules or spheroids. The ductile cast irons are the most ductile of the cast irons.
- High-silicon cast irons (over 14% silicon) are brittle, but are highly corrosion resistant in many environments. Some of the high silicon cast irons also have additions of chromium that further increase their corrosion resistance. The high silicon cast irons are widely used for corrosion-resistant castings and for anodes in impressed-current cathodic protection systems.
- Alloy cast irons have also been developed for improved resistance to corrosion and elevated temperature service. Additions of copper improve resistance to sulfuric acid and to atmospheric exposure. Highly alloyed cast irons containing nickel and chromium are also very corrosion resistant in many environments. "Ni-Resist" cast irons are very ductile and are widely used in corrosion-resistant castings, such as in pumps and turbines. "Ni-Hard" cast irons are white cast irons with high alloy content and have good resistance to erosion in some environments.

Cast iron is commonly found in boiler systems, valves and fitting, and pumps. It is subject to various form of corrosion. These include but are not limited to: general attack, graphitic corrosion, tuberculation in water boxes, and microbiological attack by sulfate reducers and acid producers.

## 6.4 COPPER ALLOYS

Copper alloys combine corrosion resistance with high thermal and electrical conductivity. They are very easy to form and fabricate. There are a large number of copper alloys, with wide ranges of mechanical properties and corrosion resistance.

Strictly speaking, brasses are copper-zinc alloys and bronzes are copper-tin alloys. However, common names can be misleading. Naval brass and Roman bronze are the same alloy. This illustrates why UNS alloy numbers are useful.

Most copper alloys are used for their corrosion resistance rather than for their strength.

### 6.4.1 Characteristics Of Copper Alloys

The corrosion resistance of copper alloys is primarily due to the noble position of copper in the galvanic series. Because it is below hydrogen in the galvanic series, copper tends to be stable in aqueous environments.

The presence of oxidizers, such as nitric acid or oxygen, can cause copper to corrode in aqueous solutions.

In some aqueous solutions, a passive oxide film is formed on copper alloys. If stable, this film can reduce corrosion. The film can be removed by high velocity flow; thus, copper alloys are generally subject to erosion-corrosion in high-velocity flow conditions.

Copper alloys can also be attacked in aqueous solution by carbon dioxide, acids, chlorides, and sulfides.

In mild atmospheric environments, many copper alloys become coated with a thin protective layer of corrosion products called a patina. This patina can reduce the corrosion rate of the alloy to very low levels and has a pleasing appearance. Sulfur compounds in industrial atmospheres and chlorides in marine atmospheres tend to inhibit formation of this patina.

Ammonia aggressively corrodes copper and many copper alloys. Therefore, special care is required in monitoring ammonia levels in circulating water in ammonia refrigeration plants, food processing plants and similar locations where ammonia contamination is possible and copper and copper alloys are present.

### 6.4.2 Uses and Corrosion Resistance

Copper alloys are widely used for water piping, pumps, valves, heat-exchanger tubes and tube sheets, hardware, wire, screens, shafts, roofing, tanks, and vessels. Table 4-3 lists the UNS values for common copper alloys.

**Table 4-3**

**UNS for Copper Alloys**

| Alloy | UNS |
|---|---|
| Copper | C11000 |
| Red Brass | C23000 |
| Yellow Brass | C27000 |
| Admiralty Brass | C44300 |
| Aluminum Bronze | C61000 |
| 90-10 Cu:Ni | C70600 |
| 85-15 Cu:Ni | C72200 |
| 70-30 Cu:Ni | C73000 |

Copper alloys are found in heat exchangers, chillers, fan coils, boiler systems, piping, values and fitting, and as pump components.

The forms of attack common to copper alloys are: mild general corrosion, pitting by soft waters with high carbon dioxide content, and stress corrosion cracking of brasses by ammonia. Since copper alloys are usually soft, they are subject to erosion corrosion and other forms of flow assisted attack. Selective leaching (dealloying) is common to copper alloys. Dezincification of brass is a typical example.

## 6.5 STAINLESS STEELS

Stainless steels are widely used for their corrosion resistance in many natural and chemical environments. It is important to remember, however, that there are many different stainless steel alloys, with widely varying corrosion resistances.

All stainless steels are not resistant to corrosion in all environments, and some environments are corrosive to all stainless steels. Great care must be given to the selection of the proper stainless steel for a given application.

All stainless steels contain chromium. Although chromium is an active element, ferrous alloys containing chromium passivate readily after exposure to air, and this passive film is stable in many environments. The corrosion resistance of stainless steels is dependent on the stability of this passive film, as explained in the discussion of the galvanic series in section 5.3.2. The stability of the passive film on stainless steels is enhanced by alloying the straight chromium stainless steels with other elements, particularly nickel and molybdenum.

Stainless steels are grouped into families with common characteristics, as discussed in the following sections.

### 6.5.1 Martensitic Stainless Steels

The S40000 series martensitic stainless steels are essentially straight chromium stainless steels, containing 12% to 17% chromium and minor additions of other elements. They can be hardened by heat treatment. Martensitic stainless steels are magnetic, and have moderate corrosion resistance in mild environments. They have relatively high strength and are used for valve parts and bearings, turbine blades, high temperature parts, surgical instruments, and cutlery. Martensitic alloys will crack in hot concentrated caustic.

Some common Martensitic stainless steels are S40300 (type 403), S41000 (type 410), S41400 (type 414), and S42000 (type 420).

### 6.5.2 Ferritic Stainless Steels

The S40000 series ferritic stainless steels are essentially straight chromium stainless steels with somewhat higher chromium content than the martensitic grades (12% to 30% chromium). They cannot be hardened by heat treatment. Ferritic stainless steels are magnetic. They are also difficult to weld. This family of stainless steels have moderate-to-good corrosion resistance depending on chromium content and environment. Also, some ferritic alloys have good resistance to high-temperature oxidation. The ferritic stainless steels are resistant to chloride ion stress corrosion cracking. They are used for automotive trim systems, furnace parts, turbine parts, heat exchangers, and food processing equipment. Ferritic alloys will crack in hot concentrated caustic.

Some common ferritic stainless steels are S40500 (type 405), S40900 (type 409), S43000 (type 430), S43400 (type 434), and S43600 (type 436).

### 6.5.3 Austenitic Stainless Steels

The austenitic stainless steels are the workhorses of the stainless steel family in most industrial systems. Austenitic stainless steels are in the S30000 and S20000 series. The S30000 series is based on alloys with about 18% chromium and 8% nickel; thus the term '18-8' stainless steels. Typical S30000 alloys contain 17% to 25% chromium and 8% to 10% nickel.

The S20000 series steels use manganese as a substitute for a portion of the nickel in the S30000 series-type alloys. These alloys cannot be hardened by heat treatment. They are nonmagnetic and easy to weld. Proper welding procedures are important for corrosion resistance of weldments, or welded areas. These areas are also referred to as heat-affected zones, or 'HAZ'. Austenitic stainless steels have better corrosion resistance than straight chromium stainless steels because of the stabilizing influence of nickel on the passive films. Austenitic stainless steels are highly resistant to neutral and oxidizing aqueous environments as well as to atmospheric environments.

Table 4-4 lists the UNS labels for common austenitic stainless steels.

**Table 4-4**

**Austenitic Stainless Steel Alloys**

| Alloy | UNS |
|---|---|
| Type 304 | S30400 |
| Type 304L | S30403 |
| Type 310 | S31000 |
| Type 316 | S31600 |
| Type 316L | S31603 |
| Type 317 | S31700 |
| Type 321 | S32100 |

The "L" designation indicates low carbon content intended to prevent chromium carbide formation during welding.

### 6.5.4 Stress Corrosion Cracking (SCC) of Austenitic Stainless Steels

Austenitic stainless steels are susceptible to chloride ion stress corrosion cracking (SCC) in water systems at elevated temperatures (see section 5.8.2). This is a real phenomenon that must be properly recognized. However, the problem is often misunderstood, leading to unnecessary concern over the use of commonly available stainless steels in water applications.

Because of its great industrial importance, the general problem of stress corrosion cracking has been studied intensively, but the fundamental mechanisms have not yet been fully explained. Nevertheless, on an empirical basis, the practical factors that influence SCC are well defined:

- Alloy composition: This is normally beyond the control of water treatment personnel. For information: type 316 is somewhat more resistant to SCC than is type 304; "L" grades, designed for welding, are less resistant to SCC; alloys with high nickel and molybdenum content are designed for resistance to SCC, but these are used only in high temperature, high stress environments.
- Stress: Good manufacturing practice includes annealing to relieve stresses from rolling, bending, welding, etc. where possible. However, residual mechanical stresses will always be present, and some manufacturing stresses, such as from rolling tubes into a tubesheet, cannot be relieved by annealing. Again, "built-in" stress is normally beyond the control of water treatment personnel, but it is important to be aware of possible locations in water systems, i.e. tubes and tubesheets, that can be susceptible to SCC.

- Temperature: This is very important. Chloride-induced SCC of austenitic stainless steels is rarely seen below about 200 °F, although occasional instances have been reported as low as 160 °F. Thus, cooling tower basins should not be affected. Heat exchangers with very high process inlet temperatures, such that waterside skin temperatures can approach 200 °F, can be problem areas, as well as boilers with chloride carryover into the steam.
- Chloride level: There is no absolute limit. 200 mg/L chloride is stated as a level below which SCC will not occur in austenitic stainless steels, regardless of temperature. Higher chloride levels are often seen in cooling systems, for example in HVAC systems where waterside temperatures rarely rise above 110-120 °F and where the only stainless steel present is in the basins. However, even in low chloride waters, concentration factors can create localized high chloride levels. Two examples:
    - Deposits: many cases of chloride SCC have been related to chlorides concentrating beneath deposits, as a result of localized boiling or concentration-cell corrosion (section 5 and figure 4-19).
    - Wet-dry regions: Intermittent wetting, i.e. splashing or occasional use, can lead to high concentrations of chlorides on surfaces, resulting in SCC problems. These problems are often corrected simply by changing operating procedures or designing out splash zones.

Following is a typical case history that shows what can happen to austenitic stainless steels in water service:

> A horizontal process counterflow heat exchanger, with type 304 stainless steel tubes, cooled hot gases on the tube side with shell side water. The inlet gas temperature was 268 °F; the outlet water temperature was 105 °F. Chloride levels in the water averaged 150 to 200 mg/L. The water flow rate was less than 0.5 ft/sec. The tubes failed by cracking at the process inlet (water outlet) tubesheet. Failure was from the water side. Investigation showed that the tubes were constrained by baffles and had been forced into the tubesheet, thus applying bending stresses. Also, the cracked area was covered with waterside deposits typical of localized boiling. It was concluded that the failure was the result of SCC caused by high concentrations of chloride ions beneath deposits, combined with localized bending stresses in the tubes.

Summarizing, water treatment personnel should not be overly concerned about the use of austenitic stainless steels in cooling systems. These steels are often required for process reasons, and they provide an easily treated environment free of general corrosion problems. Following are some guidelines:

- Use good water treatment and good housekeeping practices, to keep the systems free of deposits and flowing properly, with no dead legs.
- A system survey (section 10.1) will identify heat exchangers and other components with stainless steel tubes and other parts. These should be monitored and inspected regularly, especially if there is any possibility for localized concentration of water beneath deposits.
- Try to control cycles of concentration to keep basin chloride levels below about 200 mg/L.
- If this is not possible, and if the systems contain high temperature stainless steel components, consider makeup water pretreatment (chapter 2) to reduce chloride levels.

### 6.5.5 Precipitation-Hardening Stainless Steels

The family of stainless steels known as precipitation-hardening stainless steels can be heat-treated to high strengths by an aging process that does not require quenching from high temperature. Tensile strengths of up to 200 ksi (1,350 Mpa) can be achieved. These are magnetic steels. Their corrosion resistance is generally inferior to the austenitic grades but superior to the martensitic and ferritic grades.

Precipitation-hardening stainless steels are widely used where high strength and moderate corrosion resistance in mild environments is required. These alloys are susceptible to chloride ion stress corrosion cracking at high strength levels. Precipitation-hardening stainless steels are common in aerospace applications.

### 6.5.6 Duplex Stainless Steels

Duplex stainless steels are a relatively recent development. Their metallurgical structure consists of a 50:50 mixture of ferrite and austenite. Duplex stainless steels are about twice as strong as the commonly used austenitic stainless steels. They have good ductility, can be welded, and are not hardenable by heat treatment. The duplex stainless steels are magnetic. The corrosion resistance of these alloys is generally equal to or slightly better than that of the austenitic stainless steels in many environments. The ferric component makes the alloy resistant to chloride ion stress corrosion cracking.

Duplex stainless steels are used for tanks, vessels, and piping. The higher strength creates a weight advantage for tank trucks and marine tanker applications. These steels are also common in oil and gas production, and in the chemical process industry for heat exchangers and process piping.

### 6.5.7 Super-Austenitic Stainless Steels

Super-austenitic stainless steels are highly alloyed cousins of austenitic grade stainless steels. They contain the highest amounts of chromium and nickel, plus 4 to 6 percent molybdenum and nitrogen to further stabilize passive films.

Many of these alloys are not really steels, because they contain less than 50 percent iron. They are more corrosion resistant, especially to pitting and crevice corrosion in chloride-containing environments, than ordinary austenitic stainless steels. Super-austenitic stainless steels are more resistant to chloride ion stress corrosion cracking, and they are about 50% stronger than austenitic stainless steels.

The super-austenitic grades are used for tanks, pumps, heat exchangers, piping, and valves, particularly in chloride-containing environments, such as seawater. Two common alloys are: AL6XN (UNS N08367) and 254 SMO (UNS S31254).

## 6.6 GALVANIZED STEEL

This section is a brief introduction to galvanized steel and white rust. See the references at the end of this chapter, including the AWT paper on white rust, for more information.

Galvanized steel is simply carbon steel with a bonded coating of metallic zinc. Galvanized steel is widely used in the water treatment industry, for construction of metal cooling towers and for water-carrying pipes. It is low in cost, easily handled and with proper care, it provides long term corrosion protection for steel.

### 6.6.1 Manufacturing Methods

Galvanized steel is prepared in three different ways:

- Hot dipping, in which parts, bars or sheets are passed through vats of molten zinc.
- Mill rolling, in which molten zinc is rolled onto steel sheets, to prepare a uniform coating.
- Electroplating, normally used for small parts after forming.

Hot dipping provides the heaviest coatings, and mill rolling provides the most uniform coatings.

Historically, galvanized sheet was protected by dipping into a chromate solution to create a thin layer of zinc chromate on the surface. For environmental reasons, this process is no longer used. Zinc, therefore leaves the mill with no externally applied protection.

### 6.6.2 Corrosion Protection Mechanism

In simple terms, the zinc coating acts as a sacrificial anode (chapter 1) to protect the underlying steel. If the coating is damaged so that steel is exposed, a galvanic cell is created. Zinc, as a more active element, becomes the anode, and steel becomes the cathode. Nothing happens as long as the surface remains dry, but in the presence of moisture, a corrosion cell is created, in which the zinc corrodes and the steel is protected. This continues as long as a reasonable amount of zinc remains on the surface. When most of the zinc is gone, the remaining zinc can no longer generate enough current to protect the entire steel surface, and the steel begins to corrode.

Zinc, itself, develops a coating of zinc carbonate and zinc oxide that provides good protection against weather and water. This is the gray layer commonly seen on old galvanized steel. The coating is protective and self-healing. That is, if the coating is damaged, it will reform as long as the damage does not penetrate to the underlying steel.

Once formed, the protective coating on galvanized steel is stable in water over the pH range between about 7.0 and 8.5. Acidic and basic solutions will both attack the coating. Below pH 6 and above pH 9, both the coating and the zinc metal will dissolve rapidly. The coating is resistant to common cooling water chemicals, including normal dosages of oxidizing biocides. Very high doses of chlorine, and strong oxidants such as ozone, will attack galvanized steel.

### 6.6.3 White Rust

The protective coating on new galvanized steel does not form quickly. The time required ranges from weeks to months, depending on exposure conditions and temperature. While the coating is growing, the zinc layer is available for other reactions.

The reaction of concern involves exposure to soft water (Ca as $CaCO_3$ less than 50 mg/L) with high alkalinity (pH greater than 8.3, M alkalinity greater than about 200 mg/L). Under these conditions, a different form of zinc carbonate forms, as a paste or as white nodules rather than a protective coating. This is the material referred to as "white rust".

White rust is nonprotective, so that corrosion of zinc can continue beneath the nodules. Once started, the reaction proceeds quickly, If not corrected, a galvanized coating on sheet steel can be destroyed in a few weeks.

### 6.6.4 Correcting Existing Problems

There is only one way to correct an existing white rust problem. That is, to clean the surface and then treat the water properly to prevent further attack.

- The surface must be cleaned mechanically to remove all traces of the white deposit. This must be done carefully, using neutral pH cleaners and brushing, to avoid damaging the surface.

- If a neutral pH cleaner is used, no further immediate passivation is needed. If phosphate is not used for cleaning, the surface should be rinsed with a mixed phosphate solution at a pH of about 7.5. The total phosphate concentration can be as high as 1%, but this is not critical.
- The system can be returned to service, but the water treatment program must be adjusted as described below for new galvanized steel. This program must be continued for 4 to 12 weeks, until the zinc surface is uniformly dull gray as described above.

### 6.6.5 Preventing White Rust on New Galvanized Steel

This section refers specifically to new galvanized cooling towers.

- When a new tower is put into service, the first step must be to clean all oils and debris from the metal surfaces, using a neutral pH phosphate-based cleaner. It is best to do this mechanically, but in many cases, it will only be possible to clean the tower by circulating water. Continue circulation for at least 24 hours. If possible, drain and refill the tower. If this is not possible, simply continue with the next step.
- Begin water treatment. A phosphate-based program should always be used to start up a new galvanized steel cooling tower, regardless of what long term treatment is planned. Initial operating conditions should be pH 7.0-8.0, calcium as $CaCO_3$ 100-300 mg/L, and M alkalinity 100-300mg/L. Polymeric dispersants and copper corrosion inhibitors should be added as needed. Good microbiological control is very important. Cycles will depend upon the makeup water quality.
- This program should be continued for 3 to 6 months, or until visual inspection of the tower shows it to be gray with no white deposits.
- Again depending on the makeup water, the initial program can be continued, modified or changed completely for long-term treatment. Once a good coating is formed on galvanized steel, it will accept any treatment within the pH range specified above. HOWEVER: If an acid spill or other accident causes the pH to drop or rise far outside the 7.0 to 8.5 range, and if the galvanized steel appears visually "bright", passivation must be repeated.

New galvanized steel towers should be inspected at least annually for signs of white rust or other coating damage. Deposits should be cleaned from all surfaces to help avoid under-deposit corrosion. See the AWT Position Paper on white rust for more detailed information on this subject.

## 7.0 Mineral Scale Formation in Cooling Water Systems

Chapter 1, sections 5, 6 and 7 cover solubilities of salts in water, carbonate equilibria and theoretical aspects of mineral scale formation. These sections should be studied before reading the material in this section.

## 7.1 OVERVIEW

### 7.1.1 Definitions

The word "scale" is often used generically in the water treatment business to refer to any foreign material found in a cooling water or boiler water system. Hard, flaky deposits are called "chip scale". Dried mud deposits in cooling tower basins have been referred to as "brown scale deposits". Calcium carbonate and calcium phosphate deposits in condenser tubes are "scale deposits". The term "boiler scale" can refer to any of several different deposits that form in boiler drums, tubes and condensate lines (chapter 3).

Thus, a statement such as "the condenser tubes are scaled" says that a problem exists, but it tells nothing about the nature of the problem. This is critically important, because the corrective measures that must be taken to solve the problem, including operating procedures and chemical treatments, depend entirely upon the composition and source of the deposits.

As explained in chapter 1, the term "mineral scale" is used in this manual to refer to inorganic compounds precipitated from solution, either on a heat transfer surface or in the bulk solution. Thus, corrosion products and deposits of suspended water-born solids are not included as mineral scale.

The term mineral derives from the fact that many of the inorganic compounds that precipitate and cause problems in cooling water and boiler water systems also are found in nature as minerals. Limestone and calcite are common forms of calcium carbonate. Gypsum is calcium sulfate, and magnesium hydroxide occurs in nature as brucite. The most common mineral scale compounds found in cooling water systems include calcium carbonate, calcium phosphate, calcium sulfate, silica and magnesium silicate.

Some other compounds, although not strictly mineral scales, are formed in the same way and cause similar problems. As one example, some phosphonate compounds used as corrosion and scale inhibitors can precipitate as calcium phosphonate salts if the system is not properly controlled. These salts behave the same way as true mineral scales such as calcium carbonate and calcium phosphate.

### 7.1.2 Problems Caused by Mineral Scales

The problems caused by mineral scale formation in cooling systems are well known. They include:

- Loss of heat transfer capability: As explained in chapter 1, as little as 1/16 inch of calcium carbonate scale in a condenser or heat exchanger can reduce cooling capacity by as much as fifty percent, with obvious effects on production. Figure 4-20 shows the internal surface of a condenser tube coated with calcium carbonate scale.

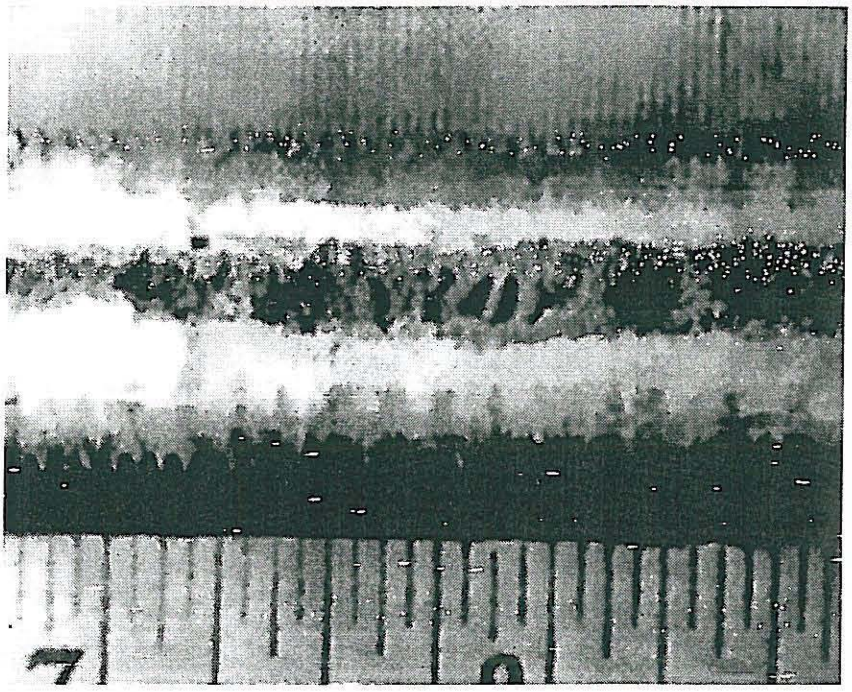


Figure 4-20. Calcium carbonate scale in a condenser tube.

- Loss of flow capacity: Massive buildup of mineral scale, usually calcium carbonate, in system piping can drastically reduce water flow, again limiting cooling capacity and production capability. In hard water areas of the country, municipal piping systems may also become plugged with heavy deposits of calcium carbonate. Figure 4-21 shows a water-carrying pipe almost completely plugged with calcium carbonate.

Figure 4-21. A water-carrying pipe plugged with calcium carbonate.

- Cooling tower damage: Film-pack fill in cooling towers (section 3.4) is made from thin, closely packed sheets of PVC. Calcium carbonate deposits can "bridge" the spaces between the sheets, thus hindering flow and reducing the cooling capacity of the tower. This fill has little structural strength and can easily collapse under the weight of calcium carbonate deposits. The fill in older splash fill towers also can collapse if calcium carbonate is allowed to collect and grow on the slats.

  Calcium carbonate often forms on the top decks of open-deck cooling towers in hard water areas. These mineral scale deposits may become heavy enough to plug the downcomer nozzles. Water then cannot flow down through the fill and is forced to overflow the sides of the tower.

- Corrosion damage: Mineral scale deposits can serve as ideal sites for localized under-deposit corrosion (section 5.0), by creating crevice areas with reduced water flow and lower levels of dissolved oxygen. Deposits on galvanized towers can lead to failure of the galvanized coating due to low localized pH beneath the deposits.

### 7.1.3 Effects on Operating Costs

The impact of mineral scale problems on cooling water system operating costs can be very significant, in terms of:

- Increased pumping costs.
- Lost production.
- Unscheduled shutdowns.
- Off-line chemical and mechanical cleaning.
- Cooling tower repairs and film-pack fill replacement.

It is universally true that the cost of a well-planned and effective water treatment program will be a small fraction of the cost of allowing the cooling system to deteriorate to failure. Water treatment is thus a good form of insurance to help protect both the equipment and facility operations.

It is also true, however, that water treatment should be the last step taken to protect the system, after all possible efforts have been made to optimize the design, operation and control of the system. Water treatment is a very costly substitute for proper operating and maintenance procedures.

## 7.2 FACTORS INFLUENCING MINERAL SCALE FORMATION

### 7.2.1 Mechanisms of Mineral Scale Formation

Mineral scale formation takes place in three stages:

- Supersaturation. Solubility and solubility products are discussed in chapter 1, section 5.0. Solids do not always precipitate immediately when the concentration exceeds the solubility product. Instead, the solids may remain dissolved in a metastable, or supersaturated, state until nucleation begins.
- Nucleation. Crystal formation begins when ions in the supersaturated solution, i.e. $Ca^{+2}$ and $CO_3^{-2}$, randomly approach each other and stick together to create a tiny crystallite, or crystal nucleus. Other ions approach and stick to the surface, and the crystal begins to grow. Nucleation will eventually start spontaneously in any supersaturated solution. The process may be "triggered" by seed crystals of the supersaturated mineral in the system, or sometimes by any foreign particle in the water that provides a surface on which crystals can begin to form.
- Crystal growth. Crystal growth is time, temperature and concentration dependent (see section 7.2.2). Crystals may grow in the bulk solution, and when they reach a critical size, precipitate as granular scale particles. Alternatively, crystals may grow attached to a metal surface. One example is the "eggshell" scale typical of calcium carbonate in condenser tubes.

  Dissolution proceeds simultaneously with growth. That is, ions dissolve (leave the crystal surface) as well as join and add to the surface. If the rate of crystallization is faster than the rate of dissolution, the crystal will grow; if not, the crystal will dissolve.

### 7.2.2 Effects of System Variables

Formation of mineral scales in cooling water systems is site-specific, depending upon water composition and operating conditions. Following are major variables that influence mineral scale formation:

- Concentrations of scale-forming ions: It goes without saying that high concentrations of precipitating ions in the bulk water, leading to supersaturation, is the primary cause of mineral scale formation. One way to prevent mineral scale formation is, therefore, to control makeup water composition and cycles of concentration to keep ion concentrations below saturation level (see temperature discussion, below).

- Ion pairs: The total dissolved ionic solids content of the water can affect solubilities of slightly soluble salts. In relatively concentrated solutions, weakly bonded ion pairs form, that effectively decrease the availability of ions to precipitate. Thus, solubilities of mineral scales may increase somewhat at high cycles of concentration, as the level of dissolved solids increases.
- Bulk water temperature: Some of the most important mineral scales in cooling water systems, e.g. calcium carbonate and calcium phosphate, are inversely soluble. That is, their solubilities decrease as the temperature increases (see chapter 1). Thus, these scales are most likely to appear first at the hot water exit end of a condenser rather than the cold water inlet. The solubility of calcium sulfate increases with temperature up to 104°F, and then decreases as the crystalline form changes. The solubility of amorphous silica increases with temperature, but silicates, such as magnesium silicate, are inversely soluble.
- Heat flux: The temperature of the thin film of cooling water adjacent to the metal surface in a condenser tube is higher than the temperature of the bulk water flowing through the tubes. Thus, inversely soluble mineral scales tend to nucleate in these films and grow on the hot metal surfaces.
- pH: Calcium and magnesium carbonates (salts of carbonate alkalinity), plus calcium phosphate and magnesium silicate, all become less soluble as the pH increases. Thus, attempts to control corrosion by increasing the pH of the water (section 5.0) must take into account the possibility of increasing mineral scale formation. The solubility of calcium sulfate is mostly independent of pH, while amorphous silica becomes more soluble with increasing pH.

  Also, the high pH that exists at cathodic corrosion sites (section 5.0) encourages mineral scaling. This explains why systems with high corrosion rates often show increased mineral scaling compared to well controlled systems.

Acid feed to keep mineral scales soluble was historically the standard method for controlling mineral scale formation. This approach is still used in many large cooling tower systems, particularly in the electric utility industry. However, two factors: the need to use alkalinity to assist with corrosion control (section 5.) and the desire to avoid handling sulfuric acid, now require most cooling towers to operate without pH control. This, in turn, requires the use of specially-designed chemicals to help control mineral scale formation (section 7.3).

- Flow velocity: If flow velocities in condenser tubes are below about 3 ft/sec., laminar flow conditions may exist. Laminar flow is less effective than turbulent flow in transferring heat from tube surfaces to the water. This causes water films on the metal surface to be thicker and hotter under laminar flow conditions, leading to higher rates of mineral scale formation. Also, slow laminar flow encourages settling and deposition of suspended solids that can bond with mineral scales on surfaces.

## 7.3 CHEMICALS FOR MINERAL SCALE CONTROL

Mineral scale control is a vitally important part of cooling water treatment technology. Operating factors that contribute to mineral scaling problems are discussed in section 7.2.2. In addition, environmental problems and regulations combine to encourage mineral scale formation in cooling systems. These factors include:

- Limitations on the use of acid to increase mineral solubilities.
- Limitations on discharge of cooling water blowdown. This forces operators to operate cooling towers at higher cycles of concentration, which in turn can increase the degree of supersaturation of scale-forming minerals.
- Water shortages, leading again to higher cycles and to the use of poorer quality water (harder and sometimes contaminated) supplies as makeup.
- Increasing use of municipal wastewater as cooling tower makeup.

Fortunately, chemical additives are available that can effectively inhibit mineral scale formation, even under severely scaling conditions. Additives stabilize supersaturated solutions, interfere with crystal growth mechanisms and help to prevent precipitated solids from attaching to metal surfaces. These mechanisms are discussed in the following sections in this chapter.

### 7.3.1 The Threshold Effect

Some chemicals, because of their molecular structures, may become incorporated in growing crystals during the initial nucleation process. Crystallites formed in this way have abnormal surface structures, and therefore do not grow regularly along all crystal faces. As explained in section 7.2.1, crystallization is a dynamic process. Ions both join and leave the crystal surfaces. If the growth process is inhibited, dissolution will predominate, so that these abnormal crystallites tend to dissolve before they become large enough to precipitate and form scale.

As the crystallites dissolve, they release the additive molecules initially trapped during nucleation. These molecules thus become available to repeat the process with another nucleating crystal. This is called the threshold effect. Dosages of chemicals much lower than stoichiometric (chemically equivalent) levels can delay nucleation of scale-forming chemicals in supersaturated solutions. In effect, this stabilizes the solution. Thus, substoichiometric dosages of only a few mg/L can stabilize solutions containing several hundred mg/L of a mineral scale such as calcium carbonate or calcium phosphate.

The threshold effect is temporary. The actual equilibrium solubility of the mineral is not changed, so that given sufficient time, precipitation will occur. However, with proper selection of additives and operating conditions, threshold stabilization can effectively prevent mineral scale formation during the normal holding (residence) time in many cooling water systems.

Additives that behave in this way are called threshold scale inhibitors. Several different types of chemicals show threshold properties:

- Some inorganic chemicals, especially polyphosphates.
- Naturally occurring lignins and tannins, and their sulfonated derivatives.
- Synthetic organic phosphorus compounds called phosphonates and phosphinates. These compounds contain phosphorus in either the +5 or +3 valence state, and they all contain direct carbon – phosphorus (C-P) covalent (nonionizing) bonds.
- Some low molecular weight (less than about 5,000) water soluble polymers of acrylic acid, maleic acid and other similar compounds.

Polymers are organic or inorganic compounds containing repeating groups of simple molecules called monomers. Homopolymers contain only one monomeric repeating chemical group. Polyacrylic acid is a typical homopolymer. Copolymers and terpolymers contain two or three, sometimes even four different monomers. By varying the types and relative amounts of these monomers, as well as the physical structure of the molecule (straight chain, branched chain, cyclic, etc.), polymeric molecules can be designed with optimized structures and activity for controlling specific mineral scales.

### 7.3.2 Crystal Growth Modification

Sometimes, distorted crystallites formed as described in section 7.3.1 survive and continue to grow. However, crystals formed in this way often do not show normal crystal structures, or "habits". Instead, the habits may be distorted into unusual shapes. For example, Figure 4-22 contains photographs of normal cubic crystals of calcium carbonate and distorted crystals formed in the presence of a scale inhibitor.

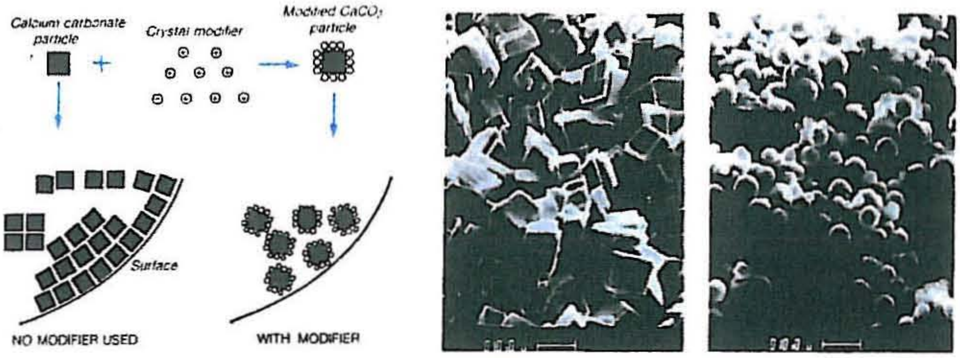


Figure 4-22. Photographs of Normal and Distorted Calcium Carbonate Crystals

The distorted crystals may take the form of another, less stable crystalline form of the same chemical compound. Thus, in Figure 4-22, the normal calcium carbonate crystals are cubic, while the distorted crystals are spherical. The spherical form is vaterite, an alternative form of calcium carbonate that is stable at higher temperatures, but not under cooling water conditions. These two forms of calcium carbonate have identical chemical compositions but very different physical properties.

Because the distorted crystals formed in this way are not thermodynamically stable under cooling water conditions, they tend to dissolve and reform, thus repeating the cyclic process. The distorted crystals therefore do not remain in the system for long and do not form either granular precipitates or scales in condenser tubes.

Chemicals that show activity as crystal growth modifiers are usually specific low molecular weight polymers. Phosphates, phosphonates and natural lignins and tannins are less effective in this form of mineral scale control.

### 7.3.3 Dispersants for Mineral Scale Control

Threshold and crystal distortion treatments can delay formation of calcium carbonate and calcium sulfate crystals, but they do not change the equilibrium solubilities. Thus some crystallization may gradually occur, especially in long holding time systems. Also, some minerals do not respond well to threshold stabilization or crystal distortion.

Chemicals called dispersants can be used in these cases to help prevent crystals from adhering to metal surfaces to form scale. Dispersants are thought to work by adsorbing on the surfaces of crystals and increasing the net negative surface charges, so that the crystals do not adhere easily to themselves or to metal surfaces. These crystals can thus be maintained in suspension in flowing water and removed with blowdown. Dispersants effective for mineral scale control are usually natural organic compounds or simple synthetic homopolymers and copolymers. Polymers that act as threshold scale inhibitors often are also good dispersants. Dispersants in cooling water treatment are discussed in more detail in section 8.0.

### 7.3.4 Synergistic Effects

The four main problems that occur in cooling tower systems (corrosion, mineral scaling, microbiological fouling and general deposition) are all interrelated, so that the presence of one problem can make other problems worse. For example:

- Corroding systems are especially prone to mineral scaling, because as explained in section 7.2.2, the high pH levels at cathodic sites causes bicarbonate to revert to carbonate (chapter 1) and form calcium carbonate.
- Microbiological slime (biofilm, section 9.0) acts as a form of "glue" to help bind other deposits to heat transfer surfaces.
- Any deposit that restricts water flow beneath the deposit can become a site for localized under-deposit corrosion or pitting, and for anaerobic microbiological growth leading to microbiologically influenced corrosion (MIC).

Because of these relationships, it is important to take an overall systems approach to designing chemical treatment programs. The nature of the system, operating restrictions, water chemistry and blowdown discharge restrictions may all play important roles in defining cooling water problems and needs for chemical treatment. Thus:

- In Los Angeles, CA, where the makeup water may be relatively noncorrosive but very hard and scale-forming, mineral scale control may be the primary focus of the chemical treatment program.
- In New York City, with soft, corrosive water, corrosion control will come first. In both cities, biofouling, if not controlled, will make all problems much worse (section 9).
- Also in New York, if corrosion is not well controlled, cathodic pH levels may rise high enough to create a mineral scale problem. This must then be controlled by a combination of better corrosion and mineral scale control.

## 7.4 CALCIUM CARBONATE SCALE CONTROL

Calcium carbonate is the most common scale found in cooling water systems. Calcium and bicarbonate alkalinity are both needed in order to form this extremely tenacious scale (alkalinity is the total concentration of $HCO_3^-$, $CO_3^{2-}$, and $OH^-$ ions present in the water, see chapter 1). An increase in temperature and/or pH will cause the bicarbonate ion to decompose to form calcium carbonate and carbon dioxide.

$$Ca(HCO_3)_2 + \text{heat} \rightarrow CaCO_3\downarrow + CO_2\uparrow + H_2O \qquad (4\text{-}27)$$

$$Ca(HCO_3)_2 + 2OH^- \rightarrow CaCO_3\downarrow + CO_3^{-2} + 2H_2O \qquad (4\text{-}28)$$

Calcium carbonate is inversely soluble (chapter 1), so that the greatest concentration of $CaCO_3$ will occur at the hottest areas along the heat transfer surfaces.

### 7.4.1 The Langelier and Ryznar Indices

Many methods have been proposed to predict the formation of calcium carbonate. They are all empirical expressions based upon the thermodynamic equilibria of carbonic acid and alkalinity, corrected for temperature and dissolved solids (ionic strength). The technical basis for these indices is explained in chapter 1.

The most commonly used equation or index for predicting calcium carbonate saturation is the Langelier Stability Index (LSI). The LSI is defined as:

$$LSI = pH - pH_s \tag{4-29}$$

where pH is the actual measured pH in the water, and $pH_s$ is the pH of saturation for calcium carbonate, calculated from the empirical expression:

$$pH_s = (pK_2' - pK_{sp}) + pCa + pAlk \tag{4-30}$$

In equation (4-30):

- $K_2'$ is the apparent second dissociation constant of carbonic acid.
- $K_{sp}$ is the apparent solubility product of calcium carbonate.
- $pCa = -\log_{10}[Ca^{+2}]$ in moles per liter.
- $pAlk = -\log_{10}$ (total alkalinity) in equivalents per liter.

See chapter 1 for an explanation of chemical equilibrium expressions.

A number of methods have been developed for estimating $pH_s$ for LSI calculations. One simple method is illustrated in equation (4-31):

$$pH_s = (9.3 + A + B) - (C + D) \tag{4-31}$$

Values for the factors A, B, C and D are selected from Table 4-5:

### Table 4-5
### $pH_s$ Calculation Factors for Equation (4-31)

| Total Solids | A | Ca as $CaCO_3$ | C | M Alkalinity | D |
|---|---|---|---|---|---|
| 50-400 | 0.1 | 10-11 | 0.6 | 10-11 | 1.0 |
| 400-1000 | 0.2 | 12-13 | 0.7 | 12-13 | 1.1 |
| 1000-5000 | 0.3 | 14-17 | 0.8 | 14-17 | 1.2 |
| **Temp °F** | **B** | 18-22 | 0.9 | 18-22 | 1.3 |
|  |  | 23-27 | 1.0 | 23-27 | 1.4 |
| 32-34 | 2.6 | 28-34 | 1.1 | 28-35 | 1.5 |
| 35-42 | 2.5 | 35-43 | 1.2 | 36-44 | 1.6 |
| 44-48 | 2.4 | 44-55 | 1.3 | 45-55 | 1.7 |
| 50-56 | 2.3 | 56-69 | 1.4 | 56-69 | 1.8 |
| 58-62 | 2.2 | 70-87 | 1.5 | 70-88 | 1.9 |
| 64-70 | 2.1 | 88-110 | 1.6 | 89-110 | 2.0 |
| 72-80 | 2.0 | 111-138 | 1.7 | 111-139 | 2.1 |
| 82-88 | 1.9 | 139-174 | 1.8 | 140-176 | 2.2 |
| 90-98 | 1.8 | 175-220 | 1.9 | 177-220 | 2.3 |
| 100-110 | 1.7 | 230-270 | 2.0 | 230-270 | 2.4 |
| 112-122 | 1.6 | 280-340 | 2.1 | 280-340 | 2.5 |
| 124-132 | 1.5 | 350-430 | 2.2 | 360-440 | 2.6 |
| 134-146 | 1.4 | 440-550 | 2.3 | 450-550 | 2.7 |
| 148-160 | 1.3 | 560-690 | 2.4 | 560-690 | 2.8 |
| 162-178 | 1.2 | 700-870 | 2.5 | 700-880 | 2.9 |
| 178-194 | 1.1 | 880-1,000 | 2.6 | 890-1,000 | 3.0 |
| 194-210 | 1.0 | 1,000-1,200 | 2.7 | 1,000-1,200 | 3.1 |

Slide rules have been developed to further simplify calculations of the LSI and the related Ryznar Index. The Ryznar Index is another empirical expression, derived from the LSI, to provide better prediction of calcium carbonate scaling tendencies in high pH waters, for example lime softened water (chapter 2):

$$RI = 2pH_s - pH \qquad (4\text{-}32)$$

where pH and $pH_s$ have the same meanings as in the LSI calculation. Figure 4-23 shows a typical slide rule that is readily available for calculating LSI and RI values.

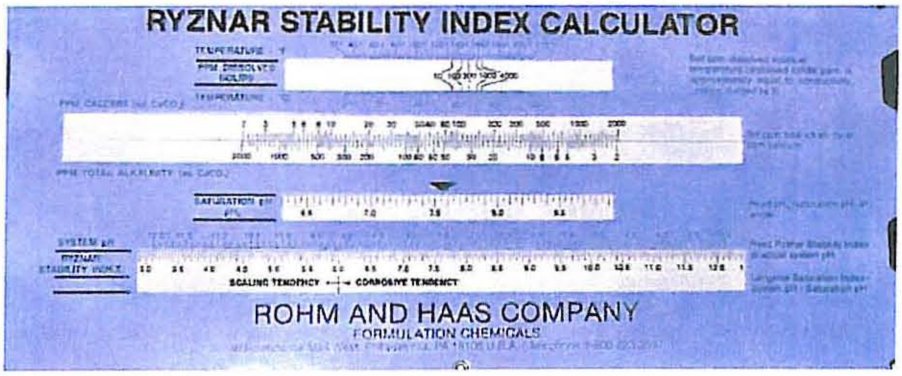


Figure 4-23. An LSI and RI slide rule calculator.

Computer programs are also available for these calculations. LSI and RI values calculated from these programs make use of actual thermodynamic solubility data rather than empirical values, and therefore tend to be more accurate. Computer-calculated values of LSI and RI are often 0.2 to 0.3 units lower than slide rule values.

### 7.4.2 Sample Calculations and Interpretation of LSI and RI Data

As explained in chapter 1, a positive LSI value indicates that the water is supersaturated with respect to calcium carbonate, so that calcium carbonate should precipitate. It says nothing about whether or not scale will actually form, or how much will form. These are site-specific factors as explained in section 7.2.2. A zero LSI value (0) indicates balanced or equilibrium conditions, and a negative value (-) indicates undersaturation – that is, calcium carbonate will dissolve. Older usage of the LSI stated that negative values indicated corrosive conditions, but this does not apply to cooling water (see chapter 1). In fact, waters with positive LSI values can be very corrosive, especially if scale inhibitors are used to inhibit formation of calcium carbonate scale.

Following is a sample calculation illustrating the use of equation (4-31) for calculating LSI and RI values:

Example: Calculate the LSI for a cooling water having the following analysis:

| | |
|---|---|
| Calcium as $CaCO_3$ | 250 mg/L |
| Total Alkalinity (M) as $CaCO_3$ | 150 mg/L |
| Total dissolved solids (TDS) | 475 mg/L |
| pH | 7.8 |
| Temperature | 125°F |

Calculations: $LSI = pH - pH_s$

From Table 4-4:

$pH_s = (9.3 + A + B) - (C + D)$

| | |
|---|---|
| A = Total Dissolved Solids | 0.2 |
| B = Temperature °F | 1.5 |
| C = Calcium as $CaCO_3$ | 2.0 |
| D = Total Alkalinity as $CaCO_3$ | 2.2 |

$$\begin{aligned} pH_s &= (9.3 + A + B) - (C + D) \\ &= (9.3 + 0.2 + 1.5) - (2.0 + 2.2) = 6.8 \\ LSI &= pH - pH_s = 7.8 - 6.8 = +1.0 \end{aligned}$$

General guidelines for interpreting the LSI and RI are shown in Table 4-6.

### Table 4-6
### Guidelines for Interpreting the LSI and RI

| LSI | RI | Conditions |
|---|---|---|
| 3.0 | 3.0 | Very strong tendency to form $CaCO_3$ scale. |
| 2.0 | 4.0 | Strong tendency to form $CaCO_3$ scale. |
| 1.0 | 5.0 | Moderate tendency to form $CaCO_3$ scale. |
| 0.5 | 5.5 | Slight tendency to form $CaCO_3$ scale. |
| 0.2 | 5.8 | Very slight tendency to form $CaCO_3$ scale. |
| 0.0 | 6.0 | Stable water |
| -0.2 | 6.5 | Very slight tendency to dissolve $CaCO_3$ scale. |
| -0.5 | 7.0 | Slight tendency to dissolve $CaCO_3$ scale. |
| -1.0 | 8.0 | Moderate tendency to dissolve $CaCO_3$ scale. |
| -2.0 | 9.0 | Strong tendency to dissolve $CaCO_3$ scale. |
| -3.0 | 10.0 | Very strong tendency to dissolve $CaCO_3$ scale. |

The LSI was originally developed for use by municipal water authorities. It is known that a thin, uniform layer of calcium carbonate scale can provide corrosion protection on steel pipe. This is a practical corrosion control method in municipal water systems where no heat transfer is involved. LSI calculations helped operators adjust the alkalinity and pH of their water supply so as to form a thin protective layer of calcium carbonate.

For convenience in doing these calculations, the positive LSI range was called "scaling" and the negative range was called "corrosive". As explained above, this is a misnomer. LSI values do not predict the corrosivity of any water. In cooling tower systems, with important temperature differences and concentrated water, waters with positive LSI values can be both scaling and very corrosive.

The correct interpretation of LSI values is "scaling" on the positive side and "nonscaling" or "dissolving" on the negative side, as shown in Table 4-6. In practice, waters with LSI values between about -0.5 and +0.5 are essentially stable to calcium carbonate.

### 7.4.3 Acid Feed for Calcium Carbonate Scale Control

As explained above, calcium carbonate scale formation can be controlled by the addition of acids to increase solubility. Sulfuric acid, which is inexpensive, is most often used. Other acids, such as hydrochloric acid, can be used when it is important to limit sulfate concentrations in the water. Sulfamic acid is convenient to handle because it is a dry chemical, but it is expensive.

Acid addition produces salts that are more soluble than $CaCO_3$. However, these salts also can reach saturation and must be controlled to prevent precipitation on heat transfer surfaces. This is especially true of calcium sulfate:

$$Ca(HCO_3)_2 + H_2SO_4 \rightarrow CaSO_4\downarrow + 2CO_2 + 2H_2O \qquad (4\text{-}33)$$

Acid feed is simple, effective and inexpensive. It is commonly used in large industrial and utility plants, but less often in commercial facilities, because of the hazards involved with handling concentrated acid. Maintaining a low pH increases the corrosivity of the water, as explained in section 5. Also, whenever acid feed is used, duplicate and backup pH control mechanisms are very important. A low pH excursion can cause damaging corrosion, and a high pH excursion in the absence of scale inhibitors can lead to immediate precipitation of calcium carbonate scale.

### 7.4.4 Inorganic Phosphates

Calcium carbonate precipitation can easily be inhibited by threshold chemical treatment and by crystal growth distortion (section 7.3). A cost-effective group of materials for this purpose is the polymeric inorganic phosphates. This class of compounds includes salts of pyrophosphate, tripolyphosphate and other polyphosphates. Concentrations are a few mg/L, which is well below the stoichiometric values required for complexing calcium hardness. The phosphates are adsorbed partly on the surface of the growing crystals and partly included in incipient crystal nuclei. A disadvantage of the polyphosphates is their tendency to hydrolyze or revert to orthophosphate, which has no scale-inhibiting properties. Orthophosphate can provide useful corrosion protection in soft water systems, but may precipitate as ferric phosphate or form calcium phosphate scale.

### 7.4.5 Phosphonates

Phosphonates are a group of organic phosphorus compounds containing direct carbon-phosphorus bonds. They are active corrosion inhibitors as well as mineral scale inhibitors, and are discussed in detail in section 5.10.6.

Phosphonates are especially effective threshold treatment inhibitors for mineral scale control, especially calcium carbonate scale, and are widely used. Concentrations are usually a few mg/L. AMP, HEDP and PBTC (Section 5.10.6) all have greater hydrolytic stability than the inorganic polyphosphates. That is, they do not decompose by reacting with water. AMP degrades readily in the presence of chlorine to form orthophosphate ions. The addition of zinc ions significantly stabilizes the AMP molecule while still maintaining its control over calcium carbonate scale. HEDP is affected less by chlorine than is AMP, while PBTC is still more stable towards chlorine. Newer commercially available phosphonate molecules also have good scale inhibiting properties and chlorine resistance.

### 7.4.6 Organic Polymers

Organic polymers also have been found to be effective calcium carbonate inhibitors. These include polycarboxylates, such as polyacrylates, polymethacrylates, polymaleates, and related copolymers and terpolymers. Treatment levels are higher than the phosphorous-bearing materials. The molecular weights of these polymers should range from 1000 to 10,000 Daltons (atomic mass units) for effective scale control.

Polymers act mostly as crystal modifiers and dispersants for calcium carbonate (section 7.3.2), whereas phosphonates act as threshold inhibitors. Polymers adsorb onto the calcium carbonate crystal structure, limiting growth and ultimately limiting scale formation. They retard calcium carbonate scaling by maintaining small particles of distorted crystalline material in suspension.

## 7.5 CALCIUM PHOSPHATE

### 7.5.1 Solubility

Calcium phosphate scale is becoming increasingly common in recirculating cooling water systems. To conserve water and energy, cooling tower systems are being operated at higher cycles of concentration. This increases the alkalinity and calcium hardness levels in the water. These factors decrease the solubilities of both calcium carbonate and calcium phosphate.

Also, phosphate levels in makeup water are increasing. Surface waters containing agricultural runoff almost always contain soluble phosphates. Secondary sewage plant effluent, containing high levels of orthophosphate ions, is a frequent source of cooling tower makeup water, especially in the electric utility industry. Also, many municipalities, large and small, now add orthophosphate, usually as phosphoric acid, to their water in order to control corrosion of old lead piping and fixtures in their systems.

Calcium phosphate is inversely soluble, but in the range between about 25 and 75°C (about 80 and 170°F) the variation with temperature is small. The solubility of calcium phosphate is a complex function of pH, calcium hardness, orthophosphate concentration, ionic strength, and temperature. Precipitates form through a chain of compounds that transform from one to another. For this reason, calcium phosphate deposits are usually amorphous when formed, but eventually transform to the more crystalline compound known as tricalcium phosphate, $Ca_3(PO_4)_2$. In boiler systems, another form of calcium phosphate called hydroxyapatite, $Ca_5(PO_4)_3OH$, precipitates as boiler sludge (chapter 3).

Calcium phosphate is substantially less soluble than calcium carbonate. Because of this low solubility ($K_{sp} = \sim 10^{-30}$, see chapter 1), deposits can form easily in waters containing as little as 5 mg/L of orthophosphate ions and 300 mg/L of calcium ions at pH 7.0 to 7.5. However, calcium phosphate supersaturates easily and precipitates slowly, even with no treatment present.

There are no reliable rule-of-thumb relationships for predicting the solubility of calcium phosphate. Computer programs that take into account both the ionic interactions and the complex precipitation reactions of calcium phosphate do a good job, but do not predict the rate at which precipitation and scale formation will occur. This is especially important in large cooling systems with long holding time indexes.

Phosphate ions in cooling water systems have other effects beyond mineral scale formation. As explained in chapter 6, orthophosphate is valuable as a corrosion inhibitor, especially in soft water systems. Polyphosphates are valuable inhibitors for calcium carbonate scale. Also, phosphate ions encourage microbiological growth and fouling (see section 9, below).

### 7.5.2 Chemical Treatment

Calcium phosphate scale is difficult to inhibit and tenacious. Once formed, calcium phosphate scales are hard to remove. Whereas calcium carbonate will dissolve quickly in even weak acid solutions at pH 4-5, much lower pH and longer contact times are required to dissolve calcium phosphate scale. This more aggressive treatment poses dangers of system corrosion unless the acid is inhibited and the process is carefully monitored and controlled.

Several different classes of compounds have been developed that can control the formation of calcium phosphate. These include acrylic acid/hydroxypropylacrylate copolymers, styrene sulfonic acid/maleic acid copolymers, acrylic acid/sulfonic acid copolymers, and phosphinocarboxylic acid/organosulfonic acid copolymers.

These compounds function both by modifying the morphology and size of calcium phosphate crystals, and by acting as dispersants to help prevent adherence of calcium phosphate to heat transfer surfaces. Moderately high dosages of these copolymers are required; for example, approximately 5-15 mg/L under conditions of moderate calcium hardness (about 500 mg/L as $CaCO_3$ with 10 mg/L of $PO_4^{3-}$ ion at pH 8.0 to 8.5). Increasing any of these parameters will require an increase in polymer concentration. An added benefit of copolymer technology for calcium phosphate scale control is that orthophosphate ions can be maintained in solution and used for carbon steel corrosion control.

## 7.6 CALCIUM SULFATE SCALE CONTROL

### 7.6.1 Solubility

Calcium sulfate can exist in various forms in cooling water systems, the most common being gypsum ($CaSO_4.2H_20$). The hemihydrate and anhydrous forms are much less common. Gypsum shows inverse solubility. That is, the solubility of gypsum decreases with increasing temperature, but the effect is much less pronounced than with calcium carbonate or calcium phosphate.

Gypsum is more soluble than calcium carbonate by at least a factor of 50. This fact provides the basis for sulfuric acid addition to control $CaCO_3$ in recirculating cooling water systems. An empirical upper limit for calcium and sulfate concentrations to avoid scale formation in the absence of a scale inhibitor can be written as:

$$[Ca^{2+}] \times [SO_4^{-2}] = 500,000 \text{ or } 5x10^5 \qquad (4-34)$$

where the bracketed values are the ionic concentrations expressed in mg/L. If the calcium concentration is expressed as calcium carbonate, as is often the case, equation (4-34) becomes, as an approximation:

$$[CaCO_3] \times [SO_4^{-2}] = 1,300,000 \text{ or } 1.3\times10^6 \qquad (4\text{-}35)$$

### 7.6.2 Chemical Treatment

Calcium sulfate scale can be controlled effectively with polyacrylates, their copolymers, and phosphinocarboxylates. As with calcium carbonate, excellent threshold inhibition can be achieved with polymers having low molecular weights in the range of 1,000 to 10,000 Daltons. Chemical treatment of a few mg/L can increase the apparent solubility of calcium sulfate (gypsum) by a factor of 20. This amounts to increasing the $[Ca^{2+}][SO_4^{2-}]$ ion product in equation (4-34) from 500,000 to 10,000,000, or $10^7$. These polycarboxylates are stable over a wide range of pH and temperature. The basic mode of calcium sulfate scale inhibition with polymers is through a combination of threshold inhibition, crystal distortion and dispersion.

Another chemical that controls calcium sulfate precipitation efficiently is the phosphonate AMP. Very low concentrations of AMP are needed, usually less than 1mg/L.

## 7.7 SILICA AND MAGNESIUM SILICATE SCALE CONTROL

### 7.7.1 Solubility

Silicon dioxide, commonly known as silica, $SiO_2$, is present in most natural water supplies, at concentrations ranging from less than 1 to over 50 mg/L. Silica hydrolyzes (reacts with water) to form silicic acid, $H_2SiO_3$. Silicic acid is a very weak acid that ionizes only above about pH 8. See chapter 1 for information on strong and weak acids.

Above pH 8, silica is present in water mostly as the silicate ion, $SiO_3^{-2}$. At lower pH levels, silicic acid begins to polymerize, forming mixtures of polysilicates and unionized silicic acid. As the pH drops, the silica polymers increase in molecular weight. The solubility decreases and silica polymers precipitate as an amorphous glassy film on heat transfer surfaces.

Silica also presents a mineral scale problem in alkaline systems when the water contains magnesium and calcium hardness. Above pH 8.5, magnesium silicate can form as a reaction product of magnesium hydroxide and silicic acid:

$$Mg(OH)_2 + H_2SiO_3 \rightarrow MgSiO_3\downarrow + 2H_2O \qquad (4\text{-}36)$$

Equation (4-36) is a general representation of the reaction, but may not describe what actually happens on the scaling surface. The reactions are complex, and the scale may, in fact, be a mixture of magnesium hydroxide, silicic acid, magnesium silicate and other compounds. The scale is glassy and amorphous, similar in appearance to low pH silica scale. Calcium silicate is more soluble than magnesium silicate, but may form above pH 8.5 if high levels of both calcium and silica are present (see below for guidelines).

Silica and magnesium silicate scales are transparent, and can easily be missed on visual tube inspections. These scales are very tenacious, dense, and difficult to remove from heat transfer surfaces. They are good insulating materials that can create high resistance to heat transfer. Cleaning requires high-pressure hydroblasting or cleaning with hydrofluoric acid, both of which can damage tubes and related equipment. Hydrofluoric acid is dangerous to handle and cannot be discharged to the environment. In some cases, managers have opted to replace heat exchanger bundles rather than attempt to remove silica scales.

### 7.7.2 Rules-of-Thumb and Chemical Treatment

Clearly, it is much easier to prevent silica scale formation than it is to recover after a silica scale has formed. The first, and most effective, line of defense is to limit the concentration of silica in the circulating cooling tower water. Table 4-7 lists empirical rules-of-thumb for silica control in open cooling systems:

**Table 4-7**

**Rules-of-Thumb for Silica Scale Control in Open Cooling Water Systems**

| Condition | Control |
|---|---|
| pH<7.5 | $SiO_2$ at 150-180 mg/L, or ($Mg^{2+}$ mg/L) x ($SiO_2$ mg/L) < 17,000 |
| pH 7.5 to 8.5 | $SiO_2$ at or below 150 mg/L; or ($Mg^{2+}$ mg/L) x ($SiO_2$ mg/L) <12,000; or ($Mg^{2+}$ mg/L) x ($Ca^{2+}$ mg/L) x ($SiO_2$ mg/L) < $3 \times 10^6$ |
| pH>8.5 | ($Mg^{2+}$ mg/L) x ($SiO_2$ mg/L) < 6,000; or ($Mg^{2+}$ mg/L) x ($Ca^{2+}$ mg/L) x ($SiO_2$ mg/L) < 90,000 |

The guidelines in Table 4-7 are based on experience and are very conservative, particularly concerning magnesium. The reason for this is that magnesium silicate scale can be devastating, sometimes requiring complete replacement of expensive equipment. Other, more liberal guidelines are available. Each system is unique because of the many interacting factors that influence silica solubility. Individual experience with specific water supplies is the best guide. As a rule, it is good advice to keep silica and magnesium levels in the circulating water well below guidelines.

Chemical treatment for silica scale control is not as successful or reliable as treatment for calcium carbonate or calcium phosphate. With the aid of specially developed polymeric dispersants, cooling systems are operating today with silica levels approaching 300 mg/L, pH control above 8 and low magnesium levels. These results should be considered experimental, even with chemical treatment in place. Control ranges above the guidelines in Table 4-7 should be approached slowly and cautiously, with careful analytical control to be sure that silica does not precipitate.

# 8.0 Fouling

## 8.1 DEFINITIONS

### 8.1.1 Deposits

The term "deposits" as used in cooling water systems, refers to any water-born insoluble matter found in heat exchanger tubes, piping systems, cooling tower basins and fill, and other system components. "Foulants" is another term used in the same way.

Corrosion products, mineral scales, and microbiological matter are all deposits, or foulants. These deposits are formed in the system by chemical and microbiological reactions, as explained in sections 6, 7 and 9 in this chapter. This section covers nonreactive deposits carried into the system with the air and makeup water, or introduced through process leaks. Such deposits include, for example:

- Particulate matter scrubbed from the air, including clay, construction debris, insect parts, etc.
- Migrated corrosion products from the system, and iron oxides formed from soluble iron carried in with the makeup water.
- Silt, clays and sand suspended in the makeup water.
- Organic contaminants, including pollutants carried in with the makeup water.
- Process leaks (oils). Note: Process leaks may also introduce soluble organic contaminants, acids, etc.
- Macrobiological matter, including such diverse substances as leaves, twigs, and wood fibers from cooling towers.
- Floc carry-over from clarifiers.

### 8.1.2 Fouling

Fouling, or deposition, is the result of deposit formation in a cooling system. Again, corrosion products, mineral scales and microbiological slimes are all foulants. This section covers fouling created by nonreactive materials such as described above. These deposits are formed by simple settling in the system. They are usually loose and porous, so that they can be dispersed or flushed away. However, in many cases, especially when silt and clay are involved, or when the deposits also contain microbiological slimes formed in the system, the deposits can be tenacious and hard to move.

## 8.2 PROBLEMS CAUSED BY FOULING IN COOLING WATER SYSTEMS

### 8.2.1 Loss of Flow

Fouling can reduce heat transfer by interfering with the flow of cooling water, sometimes to the extent that heat exchanger tubes and small diameter piping can be completely plugged. High flow rates (5 to 8 ft/sec) can often sweep away ordinary deposits. At the other end, low flow rates (less than 2 ft/sec) encourage suspended matter to settle out and form deposits. These low velocity conditions exist, for example, in shell-side heat exchangers, compressor jackets, water boxes, furnace doors and hoods, and in cooling tower basins.

Figure 4-24 shows a cooling water intake screen fouled with a combination of biomass and other debris from the makeup water. Fouling like this can limit water flow through the system. Also, much of this debris will pass through the intake screens and become a fouling problem in the system.

Figure 4-24. A fouled cooling water intake screen.

Loss of water flow can be a serious problem, both in terms of lost production or cooling capacity and in terms of recovery. If little or no water can circulate through the fouled equipment, the use of dispersants and chemical cleaning is not possible. Mechanical cleaning or replacement of pipes, tubing and equipment may be the only options. It is therefore very important not to allow fouling conditions to progress to this extent. In most cases, loss of flow will become obvious long before the system is plugged, so that corrective actions can be taken (see below).

### 8.2.2 Loss of Heat Transfer Efficiency

Just as with corrosion products, mineral scales and microbiological slimes, general fouling deposits can interfere with heat transfer by creating barrier layers on heat exchange surfaces. These deposits are often loose and porous, and hold large amounts of water. Water has a high heat capacity compared to metals (chapter 1). A thin trapped layer of water in a heat exchanger, for example, can cause severe loss of cooling or heating capacity, requiring more energy input to maintain normal production.

## 8.3 MECHANICAL METHODS FOR FOULING CONTROL

### 8.3.1 Water Flow Velocity

Control of water flow velocity can be used in several ways to help prevent fouling and to clean previously fouled equipment:

- As explained in section 8.2.1, control of operating conditions to maintain flow rates of roughly 3 to 8 ft/sec. in heat exchangers and small diameter piping is the first line of defense in preventing general deposition in cooling water systems. Below 3 ft/sec, settling becomes important, and above about 8 ft/sec, erosion-corrosion can occur, especially on softer metals such as copper.
- Sudden brief changes in velocity can be effective in helping to loosen and remove deposits. If it is not practical to maintain good flow velocity in a system, sudden opening of throttling valves for a brief time can dislodge and move loosely settled material.
- Backflushing (reversing flow direction through a heat exchanger, furnace hood, etc.) can also help to move deposits. Process heat exchangers are often piped to make backflushing a routine operation.
- Air bumping – injecting slugs of compressed air – is effective in moving loosely settled deposits. Check to be sure that there are no pumps or other equipment that can be airbound downstream of the injection point.
- In industrial plants, a process called "shotgunning" – that is, shooting single slugs of water through tubes under pressure – can remove loose material but not smooth, adherent deposits such as mineral scales.
- Finally, hydrolazing – cleaning of heat exchanger tubes with water streams at 1,000 to 10,000 psig – is an effective method of removing most deposits. Hydrolazing always involves danger of mechanical damage to tubes, particularly soft metals such as brass and copper.

### 8.3.2 Tube Brushing

Figure 4-25 illustrates some of the mechanical methods commonly used to clean condenser tubes, including brushes, sponge balls and scrapers.

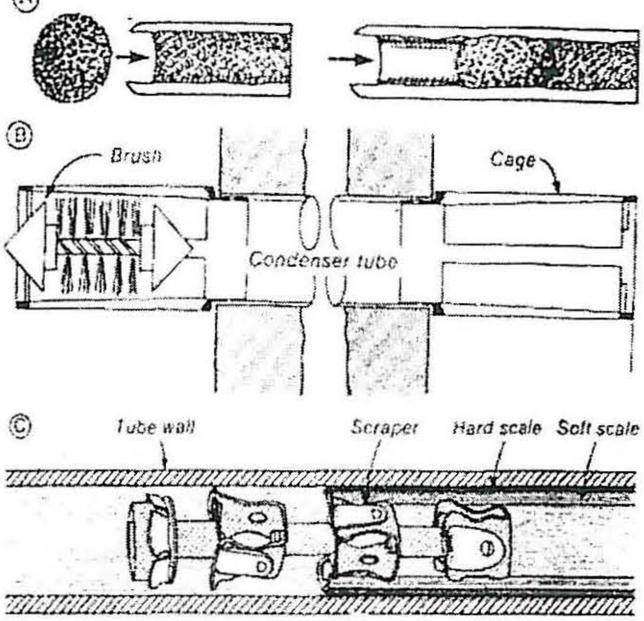


Figure 4-25. Mechanical methods for cleaning condenser tubes:

a) sponge balls; b) brushing; c) scraping

Condensers in HVAC systems and electric power stations are commonly brushed during annual inspections or outages. Brushing effectively removes loose debris, microbiological matter, tubercular corrosion products and some mineral scales. Brushing usually will not remove firmly attached, smooth corrosion products and mineral scales.

Brushes can be hand fed through tubes, driven by high pressure water, or attached to a flexible rotating motor shaft.

Brushes are normally made from nylon, and are sized and shaped to fit specific types of smooth and rifled (enhanced) heat exchanger tubes. Operators are sometimes tempted to use metal brushes in an effort to remove hard deposits. This is a dangerous practice. Protective coatings can be damaged and tubes can be scratched, leading to increased corrosion where the metal surface has been stressed. Specifically, brass brushes must never be used with steel tubes, because small amounts of brass left on the steel surface can become sites for galvanic corrosion (section 6).

### 8.3.3 Ball Cleaning Methods

Many utility systems, and some large HVAC systems, include equipment that automatically circulates rubber balls through heat exchangers to help keep the tubes clean. Balls can be hard or soft, and may have smooth or roughened surfaces. The "Taprogge System" is one such ball cleaning system that is commonly used.

Ball cleaning can help to prevent accumulation of loose sediments, but there are several drawbacks to this system. The balls will not remove hard deposits, and by wiping the metal tube surfaces, they may actually encourage formation of smooth deposits. This is especially true of microbiological slimes. Balls will remove accumulated microbiological matter, but at they same time they contaminate the entire metal surface, so that the deposits regrow quickly.

### 8.3.4 Screens and Coarse Filters

In once-through cooling systems, coarse filters (bar screens, trash racks, and traveling screens) are used to remove large debris. Similar systems are used in the intake structures for large industrial and utility circulating cooling water systems. Full flow fine particle filtration is not practical in once through systems. It is important that operators maintain their intake water cleaning equipment. Automatic flushing and screen changing equipment can fail. Also, screens may become too badly fouled for effective cleaning with automatic equipment, so that off-line manual cleaning is required.

### 8.3.5 Sand and Bag Filters

Fine particle filtration is a recommended, effective way to help remove suspended matter from open recirculating cooling water systems. As a rule-of-thumb, passing three to five percent of the recirculating water through a side-stream filter will reduce the suspended solids loading by up to 80 to 90 percent at 5 to 8 cycles of concentration. This can be a major advantage in helping to control fouling deposits in almost any system.

Sand filters are available in many different designs and sizes suitable for large and small cooling systems. Both upflow and downflow designs are practical. With specially prepared sand media and proprietary filter designs, manufacturers claim to be able to remove particle as small as 0.5 micron (0.0005 millimeter) in diameter.

Sand filters require regular backwashing to remove the accumulated solids. The filters are usually designed to backwash automatically, controlled by a timer or by pressure drop. With pressure drop control, it is good practice to include a backup timer to trigger the backwash cycle if it does not occur within a set time based on pressure drop. This helps to prevent gradual accumulation of hard, matted deposits in the filter. For best results, the filter should be backwashed with makeup water or fresh city water, rather than with circulating tower water.

Although sand filters should not require regular attention, they should be inspected regularly to ensure that they are operating properly. Filters that are not to be used for an extended period should be drained and emptied. Stagnant sand filters quickly become breeding grounds for bacteria. Operating sand filters should be chlorinated regularly, depending upon the microbiological loading in the system, and the sand should be changed every three to five years. Particle size analyses of the filter inlet and effluent waters is a good way to determine whether or not the filter is performing up to specifications.

Bag filters are also used effectively in circulating cooling tower systems. They are simpler to install and less expensive than sand filters. Bags are available in many different particle size ranges. However, bag filters require regular maintenance to replace the bags as needed, and in some cases, disposal of used bags may be a problem.

## 8.4 CHEMICAL METHODS FOR FOULING CONTROL

### 8.4.1 Dispersants

Along with sidestream filtration, on-line low level chemical treatment with dispersants is the accepted routine method for controlling fouling by settleable solids. Originally, naturally occurring compounds, such as tannins, sulfonated lignins and carboxymethylcellulose, were used, but synthetic polymers have been found to be more effective. Natural products require higher concentrations to produce good dispersion of foulants, they may not be cost effective, and they may contribute to foaming. Also, synthetic polymers are not as easily degraded by biological organisms as the natural polymers.

Polyacrylates, polymaleates, partially hydrolyzed polyacrylates, and their copolymers are now the most commonly used dispersant chemicals. These are either the same compounds described in section 7 for mineral scale inhibition, or very similar derivatives. The most important aspect of these materials is their molecular weights. Effective dispersants have molecular weights in the range of about 1,000 to 10,000 Daltons - the same range as for scale control. Concentrations of a few mg/L are required in open recirculating systems, but lower levels are normally used in once-through systems.

Although low molecular weight anionic polymers as described in the previous paragraph are most commonly used, many other types of polymers are also available. Cationic amines and quaternary amines are effective in dispersing some biological materials, and may also have biocidal properties. Nonionic polyacrylamides disperse heavy clay slurries, and at higher molecular weight also act as flocculants (section 8.4.2). Some polymers have been developed specifically to disperse common suspended solids such as calcium carbonate, calcium phosphate and iron oxides.

It is common practice to include a few mg/L of dispersant polymer in almost all open recirculating cooling water treatment programs, and in many closed system programs as well. Dispersants serve as backup protection for mineral scale control programs (section 7) and help to keep piping systems and heat exchangers clean so that corrosion inhibitors can reach the metal surfaces.

A different group of compounds, called biodispersants, is used to penetrate and loosen microbiological slimes. These compounds are not polymers. They are actually a group of low-foaming nonionic surfactants. Biodispersants are discussed in more detail in section 9.

### 8.4.2 Flocculants

Increasing the molecular weight of synthetic polymers into the million Dalton range changes their performance characteristics. Instead of dispersants, the polymers become flocculants. That is, they act as bridging, or collecting agents that gather together small, colloidally-dispersed particles to form larger, settleable particles called "flocs". These high molecular weight polymers consist of polyacrylamides, polyamines, or polyacrylates and their various copolymers. The floc particles are generally nonadherent and easily moved along by flowing water.

To settle deposits, high molecular weight polymers are usually added at concentrations of 0.2 to 0.5 mg/L to makeup water clarifiers or thickeners (chapter 2). Similar concentrations are used in open recirculating systems. However, this use is controversial. Success depends upon being able to keep the flocculated solids in suspension so that they can be removed from the system with blowdown or by filtration. Deposits will tend to accumulate in low-flow or stagnant areas in the recirculating systems, and sludge buildup in the cooling tower basins will necessitate periodic cleaning. However, experience has shown that addition of flocculants with a properly sized and designed filter system can significantly improve performance and backwash effectiveness.

## 8.5 CHEMICAL CLEANING

Sometimes cooling systems that have been in use for a long time require cleaning to remove accumulated old deposits and restore performance. Also, new systems should be cleaned before going into service, to remove oil and mill scale.

Two general methods for chemical cleaning of piping systems and heat exchangers are available:

- On-line cleaning, while the equipment is in service.
- Off-line cleaning, with the equipment out of service and drained.

The cleaning method to be used will depend upon the nature of the problem, the degree of cleaning that is required, the time frame in which the cleaning must be accomplished, and site-specific physical layout, operating constraints and discharge regulations. Also, in many critical systems, a shut-down for off-line cleaning is not possible.

The objectives of any chemical cleaning program must be carefully defined so that success or failure can be evaluated. Following are some general guidelines:

- If the objective is heat transfer improvement, then clean heat transfer surfaces must be the evaluation criteria. Success can be measured by inspections and by improved production or cooling capabilities. These are critical cleaning assignments.

- If the objective is removal of loose deposits to control under-deposit corrosion, then before and after pipe inspections are required. Fiberoptic inspection methods and spool piece inspections can be used for evaluation. As a general rule, it is not necessary to remove thin, hard, tightly adherent deposits unless they are interfering with heat transfer. These deposits provide useful corrosion protection, so that removing them may expose fresh metal to corrosion.
- If the objective is simply flow improvement, then pipe inspections and flow measurements provide evaluation data. Completely clean pipes may not be necessary. These are the least critical cleaning assignments.

This section provides an overview of the capabilities and problems involved in on-line and off-line chemical cleaning methods.

### 8.5.1 On-Line Cleaning

On-line cleaning is non-invasive. It simply involves adding cleaning chemicals to the system, continuing normal operations for a specified time, and then either briefly draining and refilling the system or gradually bleeding off the cleaning chemicals.

On-line cleaning has the advantage of being simple, relatively inexpensive and non-invasive. At the same time, it may be less effective than off-line methods. Nevertheless, it may be the only available option for restoring performance to a seriously fouled system.

On-line cleaning may be performed in two ways:

- Long term (weeks or months), using increased levels of normal dispersant chemicals (section 8.4.1). Dispersant dosages are raised to a range from 3-4 times normal maintenance level up to about 100 mg/L. Over time, dispersants may loosen silt deposits and some corrosion products. Dispersants will generally not remove mineral scale, hard corrosion products or microbiological fouling, and they will not produce a "bare metal clean" system.
- Short term (a few days to a month at most), using special cleaning formulations, usually organic acids and dispersants. Cleaning will be much more aggressive, and more effective, than with dispersants alone. In some cases, the system can be cleaned to bare metal. Plans must be in place to dispose of spent cleaning and rinse solutions, and to respond to any leaks that may appear in previously corroded threaded joints, etc. A short outage for draining the cleaning solution will normally be required, and plans must be made for proper disposal of the spent cleaning solution.

### 8.5.2 Off Line Cleaning

Off line cleaning, either of a heat exchanger or an entire cooling system, is a major project that requires careful planning and execution. It involves a draindown of the system, addition of aggressive chemicals, circulation with possible second additions of chemicals, several drain and rinse cycles, and repassivation of the system before returning to service. The time required is about 48 to 72 hours. Cleaning and first rinse waters are usually hazardous wastes that must be trucked off site. There is a definite possibility of creating system leaks at previously corroded locations.

Even with these problems, off-line cleaning is often the method of choice for cleaning severely fouled systems. The work is best done by an experienced contractor who can supply chemicals, pumps, heaters, hoses, tank trucks, monitoring tools and personnel. A working team should be established, including facility management, engineers/operators, vendor personnel and the cleaning contractor. The system should be studied carefully and the entire operation rehearsed before any cleaning is undertaken.

Personnel must be available to walk the system while cleaning is in progress, so that leaks can be spotted and clamped quickly for later permanent repair. It is especially important to ensure that the entire system to be cleaned can be circulated and drained. Any undiluted cleaning solution left in the system after cleaning is finished will cause severe damage.

### 8.5.3 Selection of Cleaning Chemicals

When planning any on-line or off-line chemical cleaning program, all materials in the system must be carefully considered. In addition to common steel pipe and copper tubes, this includes pump impellers, soldered joints, pump seals, gasketed connections, etc. Any component failures can make the entire cleaning program a disaster.

Special concern must be given to galvanized cooling towers, to protect the zinc coating. On-line cleaning of galvanized towers can be done only with neutral pH chelant or dispersant cleaners. Off-line, it is best to isolate the tower to avoid contact with aggressive chemicals. This may require additional valving and temporary pumps.

## 9.0 Microbiological Fouling

### 9.1 OVERVIEW

The presence and growth of living organic matter in cooling systems is commonly referred to as biofouling. Biofouling (biofilm) can interfere with the flow of water through heat exchangers and other conduits. This inhibits heat transfer and contributes to corrosion and general deterioration of the entire cooling system. Biofilm also serves as a "glue" to help attach and hold other deposits on surfaces.

Recirculating cooling water systems are ideal incubators for promoting the growth and proliferation of microorganisms. Waters saturated with oxygen, exposed to sunlight, maintained at a temperature of 30 to 60$^0$C, and having a pH of 6 to 9 ensure abundant nutrients and an appropriate environment for life-sustaining growth. Figure 4-8 is a good example of a microbiologically-fouled cooling tower basin. Figure 4-26 shows microbiological growths in a heat exchanger.

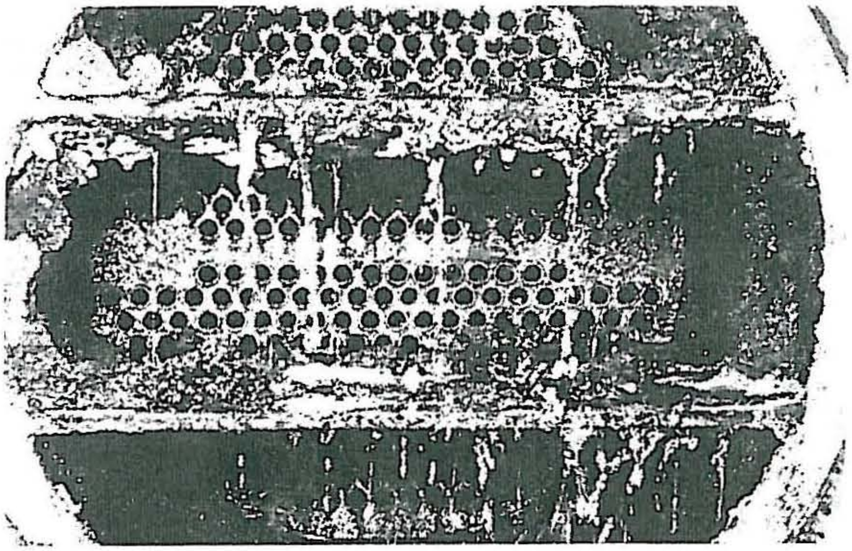


Figure 4-26. Microbiological growths in a heat exchanger.

This chapter is concerned with the types of organisms that exist in cooling water systems, the growth of biofilm, problems caused by microorganisms and biofilm, and methods for controlling the growth of microorganisms in water.

Three major classes of microorganisms are associated with recirculating cooling water systems: algae, fungi, and bacteria. Table 4-8 is a summary showing the major characteristics of these organisms and some of the problems they cause.

**Table 4-8**

**Characteristics of Commonly Occurring Microorganisms**

| Type | Problems Encountered |
|---|---|
| Algae | Green and blue-green slimy growths in lighted areas. Interferes with water distribution, heat transfer, and may accelerate corrosion. |
| Fungi | Growths encountered above water line. Form large masses of filaments, which can trap other materials and accelerate fouling. |
| Bacteria | Gray-brown slime masses of bacteria and waste materials that can plug heat exchangers, reduce heat transfer, accelerate corrosion and cause buildup of foulants. |
| Iron bacteria | Red-brown slime mass. Requires ferrous iron ($Fe^{2+}$) for growth. Deposits insoluble ferric hydroxide [$Fe(OH)_3$]. Can plug heat exchangers and piping, and reduce heat transfer efficiency. |
| Sulfate reducing bact. | Black insoluble ferrous sulfide (FeS) deposits which can plug heat exchangers and accelerate under-deposit corrosion. |

The following sections discuss each of these microorganisms in more detail.

## 9.2 ALGAE

### 9.2.1 Description

Algae are very simple plants; without roots, leaves, or stems, that grow in aqueous environments. The most important types of algae found in industrial water systems are microscopic in size, as shown in figure 4-27.

.Figure 4-27. Microscopic green algae at 400X magnification

The algal masses in figure 4-27 are relatively large, and add bulk to algae biomass deposits. Many species occur as single-celled forms (unicellular algae), which may be spherical, rod-shaped, or spiral. Other types of algae are multicellular, which appear in numerous forms and shapes, including slimy masses of several cells or long strands of filaments of cells connected together, forming specific functional structures (filamentous algae).

All algae contain colored materials called pigments. The most important of these are the chlorophyll pigments, which are responsible for the green color displayed by most forms of algae. Blue-green, brown, yellow, pink and black algae are also well known.

### 9.2.2 Growth

Algae are found almost anywhere the proper requirements for growth are present. These requirements include water, sunlight, and air, although temperature, pH, and certain chemical requirements are also important. Algae cannot grow in the absence of sunlight. Therefore, they are not normally found in closed systems. However, dead algal masses have been found plugging small diameter pipes in closed cooling loops that operate as part of free cooling systems that involve mixing condenser and chilled water systems.

Algae require an aqueous environment in which to grow because they must take dissolved nutrients in water into the cells through the cell walls. They also require contact with air or with dissolved gases in water, including oxygen and carbon dioxide. The carbon dioxide in air and water is a key factor in the metabolism of algae.

Algae are typically responsive to moderate changes in pH. Most types of algae grow over a wide range of pH in aqueous environments. pH 4.5 to 9.0 is an optimum range for many forms of algae.

### 9.2.3 Problems Associated with Algae

The primary problem associated with the growth of algae is plugging and fouling of screens, filters, and cooling tower components. The filamentous forms of algae have the capability of entraining large amounts of non-microbiological mass and, subsequently, form troublesome deposits.

Often, these deposits create a favorable environment for other types of microorganisms to grow, including bacteria and multicellular organisms such as protozoa. Unicellular forms of algae are easily washed away from the sites where they grow and are transported to other areas of the system, providing a nutrient source for bacteria and fungi. These microorganisms, using the algae as a food source, may cause slime and MIC problems. Therefore, it is generally recognized that without control of algae growth, prevention of biological slime, biological deposits, and MIC is difficult.

MIC is only one form of corrosion that can be exacerbated by the presence of algal deposits. The impact of algae on metal corrosion can be severe. The large slime masses contribute to crevice corrosion and pitting. Algae drawn into the circulating water system can lodge in heat exchangers and piping, and create sites for under-deposit corrosion.

## 9.3 FUNGI

### 9.3.1 Description

Fungi are a diverse group of plants. Unlike algae, they do not have chlorophyll and are unable to produce their own organic energy food source. Although there are many different groups of fungi, those of most concern in water treatment include molds, yeasts and wood-rotting fungi.

Most fungi are multicellular. The structure of the various types of fungi may be either unicellular or multicellular filaments with a high degree of cell differentiation. Yeasts are typically unicellular, where as molds are usually multicellular filamentous form.

### 9.3.2 Growth

Fungi cannot produce their own food by photosynthesis. Therefore, they must obtain their organic energy nutrients from non-living organic matter, or by feeding as parasites on living plant and animal substrates. Fungi are found almost anywhere the proper requirements for growth exist. These requirements include water, air, organic nutrient substrates, and essential inorganic nutrients. Fungi, in general, are not very selective concerning the source of the organic nutrient substrate. Temperature, pH, and the presence of other microorganisms also have important effects on the growth requirements of fungi.

Since fungi do not require light to produce a food source, this means that they may grow in closed-loop systems and other areas not exposed to light. As with all microorganisms, fungi require moisture or free water for growth. They can obtain water from the atmosphere, as well as from the substrate on which they are growing.

Most fungi are aerobic. Thus, when fungi grow in a water system, they are usually found at or above the water level. Some yeasts may grow aerobically or anaerobically, which enables the fermentation or degradation of organic substrates even under oxygen free conditions.

Fungi can grow over a wide pH range, from 2 to 9, with the optimum for most types being 5 to 6. Common yeasts grow well in acidic conditions, pH range from 2 to 8, and an optimum of 3 to 4.

Similarly, fungi carry on active growth over a wide temperature range (i.e., 0 to 60°C). Optimum temperatures, between 22 to 30°C, provide conditions where a wide range of fungi may become dominant in a mixed microflora. Many types of yeast also grow over a wide temperature range, 0 to 45°C, although the optimum range for most yeasts is 20 to 30°C.

### 9.3.3 Problems Associated with Fungi

Many of the problems caused by the growth of fungi are similar to those associated with algae; the primary difference is the location where the fungi grow. Since fungi do not need light to grow, they can colonize and contribute to plugging and fouling problems throughout a cooling water system. Quite frequently, filamentous fungi establish colonies, which entrain and bind suspended solids into masses that cause operational difficulties. These masses frequently are found in low-flow areas in the circulating water systems, in dead or stagnant flow areas, and on screens or filters. Often colonies of fungi develop on the surface of the fill in cooling towers, to the extent that the evaporative capacity of the tower (cooling efficiency) can be significantly reduced.

A problem caused by fungi that is often overlooked involves the situation where fungal colonies provide an optimum growth environment for other problem-causing microorganisms, particularly bacteria. Because of the fungal growth, the bacteria can grow protected from external environmental factors that would normally limit bacterial growth. Fungi also provide essential nutrients for other microorganisms in the microenvironment created by the fungal colony.

As explained above, most fungi are aerobic, so that they consume available oxygen in the microenvironment within a colony. This creates an anaerobic environment within or underneath the fungal mass, where anaerobic bacteria, such as sulfate-reducing bacteria (SRB) can live and perhaps initiate MIC. Under extreme conditions, fungi contribute to the formation of deposits that serve as a barrier to the diffusion of oxygen in the circulating water to the metal surface on which the fungal colony is attached. This creates an oxygen diffusion concentration gradient and a high potential for under-deposit corrosion.

### 9.3.4 Wood Rot

Fungi are frequently involved in the deterioration or rotting of wood. In industrial cooling water processes, the deterioration of wood cooling tower components often is ignored and not recognized as a microbiological problem.

Certain fungi can cause wood rot, called internal or "dry" rot by growing within the wood cells. The fungi produce an enzyme that attacks the cellulose, reducing it to simple sugars that are then used as an energy nutrient source by the fungus. They also produce enzymes that degrade the lignin that bind the cellulose fibers into a structurally strong element, causing loss of strength and failure of the wood components.

Other fungi grow on the surface of the wood and produce cellulose-degrading enzymes that attack the external surfaces. This is referred to as soft rot, that can contribute to microbiological plugging and fouling problems.

## 9.4 BACTERIA

### 9.4.1 Description

Bacteria are the major organisms of concern in cooling water systems. They are unicellular microscopic organisms, considerably smaller than most fungi and algae, ranging in size from 0.5 to 2.0 microns in diameter and 1.0 to 6.0 microns in length. Bacteria exist in three basic forms: rod-shaped (bacillus), spherical (coccus), and spiral (spirillus).

Aerobic bacteria absorb dissolved oxygen from water and react with carbon dioxide or other carbon forms to produce carbohydrates for food. Therefore, water or wet environments high in organic content are suitable for the proliferation of bacterial slimes. Heat exchangers are ideal incubators for this biomass. Such slimes can significantly reduce heat transfer efficiency and aggravate under-deposit corrosion.

The presence of dissolved oxygen is not required by all species of bacteria. Anaerobic bacteria grow in the absence of oxygen. These organisms obtain their metabolic oxygen by reacting with organic and inorganic oxygen-containing species in water. One well-known example is sulfate-reducing bacteria (SRB), that react with sulfate ions ($SO_4^{2-}$) to consume oxygen and liberate sulfide ($S^{2-}$).

Several other groups of bacteria exist in cooling water environments. Iron-depositing bacteria can oxidize water-soluble ferrous ions ($Fe^{2+}$) to insoluble ferric oxide ($Fe_2O_3$), which will deposit on the inside of piping, reduce flow, and aggravate crevice corrosion. Slime-forming bacteria form dense, sticky biomasses that impede water flow and contribute to fouling by sustaining the growth of other organisms.

Most bacteria possess no pigments that are directly involved in a specific physiological process. Bacteria have a rigid cell wall. The cell wall is a porous membrane that allows materials to pass in and out of the cell. Integrity of the cell wall is critical to the survival of the microorganism, since it is vitally involved in the transport of nutrients and metabolic products to and from the cell. Damage to the cell wall therefore is a primary method of killing bacteria.

### 9.4.2 Growth

Bacteria can exist in several different metabolic states. Those that are actively respiring, consuming nutrients, and proliferating are said to be in a "growth" stage. Those that simply exist, not growing because of unfavorable conditions, are said to be in a "resting" state. Some strains, when faced with unacceptable surroundings, form spores that can survive extremes of temperature and long periods without moisture or nutrients, yet produce actively growing cells quickly when conditions again become acceptable.

Many bacteria excrete exo-enzymes. These enzymes subsequently digest (hydrolyze) complex chemical compounds into simple substances, which are then able to pass through the cell wall and be used as nutrients by the bacteria.

Bacteria, like all living cells, require carbon in some form. Some bacteria require only carbon dioxide as their carbon source. Others require organic carbon compounds to supply carbon as an energy source nutrient and to supply carbon to synthesize cell structure.

The carbon source and other specific growth requirements are the basic criteria on which classification of the different types of bacteria is made. Since the cell form is so simple and cellular differentiation does not exist, the metabolism of the various types of bacteria has been studied extensively, and has been the basis for grouping bacteria into metabolic types, e.g., sulfate-reducing bacteria, acid-producing bacteria, nitrogen fixation bacteria, aerobic/anaerobic bacteria, gas-producing bacteria, sulfur bacteria, iron-oxidizing bacteria, etc. Some of these are discussed in more detail later in this section.

Bacteria are not photosynthetic and, therefore, do not require light to produce an energy source nutrient. Bacteria are typically aquatic microorganisms, requiring free water to carry on normal growth. All nutrients and metabolites must be in solution before they can enter the cell. Most bacteria therefore will thrive best in water that contains high levels of organic and inorganic nutrients.

Oxygen requirements for bacteria differ widely. Bacteria are divided into at least three different groups, based on their oxygen requirements:

- Aerobic bacteria require, without exception, the availability of free dissolved oxygen in water for metabolism and growth.
- Anaerobic bacteria can grow only in the complete absence of free oxygen. Oxygen may actually be toxic to these organisms or may it be a factor that prevents growth of the organism.
- Facultative (aerobic/anaerobic) bacteria can grow with or without free oxygen. They may use alternative metabolic processes, depending on the amount of oxygen available in the environment. In many cases, the oxygen requirements of facultative organisms are interrelated with other growth factors, such as chemical nutrients, pH, and temperature.

Bacteria can grow over a wide pH range, with 4 being the minimum for most species, and 9 the maximum. It is misleading to consider the pH of the bulk medium in which bacteria are growing as a controlling growth factor, because most bacteria create the pH of their own microenvironment. Some bacteria produce sulfuric acid as a metabolic by-product and, therefore, grow in an extremely acidic environment. Other bacteria produce ammonia and grow in a high pH environment. However, in industrial cooling water systems, bacteria generally are dominant members of the microflora when the pH is within the range of 6 to 8.

Since bacterial metabolism depends on chemical reactions. and these chemical reactions are often dependent on temperature, bacterial growth rates are partially determined by temperature. The temperature ranges of most industrial processes do not limit the survival of bacteria.

Bacteria are involved either directly or indirectly with every classification of microbiological problems such as biological slime, plugging and fouling, and microbiologically-influenced corrosion. Bacteria are components of virtually all microflora found in industrial cooling water systems, and therefore must be a major consideration in dealing with these problems.

The following sections describe some of the more common and troublesome forms of bacteria that inhabit industrial and HVAC cooling tower systems.

### 9.4.3 Slime-Forming Bacteria

Slime forming bacteria come in many varieties, but Pseudomonas is most prevalent in cooling waters. These are the most common, and one of the most troublesome, forms of bacterial contamination. Slime forming bacteria are aerobic. They grow rapidly in the presence of dissolved oxygen and nutrients. Their major metabolic product is a polymeric material that provides protection for the bacteria and for other bacteria, protozoa, etc. This is the "exo-slime" that can be felt along the inside of cooling tower basins, on corrosion coupon holders, etc. The slime collects other deposits, interferes with heat transfer and blocks flow in small diameter pipes and condenser tubes.

The slime reacts readily with oxidizing biocides. Chlorine tends to oxidize ("burn") the outside of slime masses without penetrating the slime to kill bacteria. Thus, badly fouled systems can have a high chlorine demand (section 9.5.3), but chlorine may be ineffective in killing bacteria and other organisms inside the slime. Biodispersants, surface-active chemicals that can penetrate and under-cut slime masses to lift them from the surface, are often helpful in dispersing slime layers to make the bacteria accessible to biocides.

### 9.4.4 Sulfate-Reducing Bacteria

Sulfate reducing bacteria (SRB) are anaerobic. They obtain their oxygen by reducing sulfate or other oxidized sulfur anions, to produce hydrogen sulfide ($H_2S$). Hydrogen sulfide dissolves in water and dissociates as a weak acid:

$$H_2S = H^+ + HS^- \qquad (4\text{-}37)$$

The acid corrodes the metal substrate as explained in section 5.5.3. This, in very simplified form, is the source of microbiologically influenced corrosion (MIC). MIC is seen primarily on low carbon steel, and stainless steels. However, it has been shown to be a cause of pitting corrosion on all common metals except titanium.

The form of corrosive attack on carbon steel by SRB is quite distinctive, as shown in Figure 4-14. It is recognizable by the smooth, disc-shaped concentric rings formed on the metal surface. Corrosion rates as high as 100 mpy can occur under optimum growth conditions. The formation of black iron sulfide deposits, accompanied by an odor of rotten eggs, are characteristic of attack by sulfate-reducing bacteria.

MIC caused by sulfate reducing bacteria is also common on copper alloys and on austenitic stainless steels. A special morphological characteristic of MIC on stainless steels is deep, sharp-edged pitting, as in Figure 4-28. Note the through-wall penetration in one pit. Longitudinal "worm-like" tunneling, as shown in Figure 4-29, is another morphological characteristic of MIC on austenitic stainless steels.

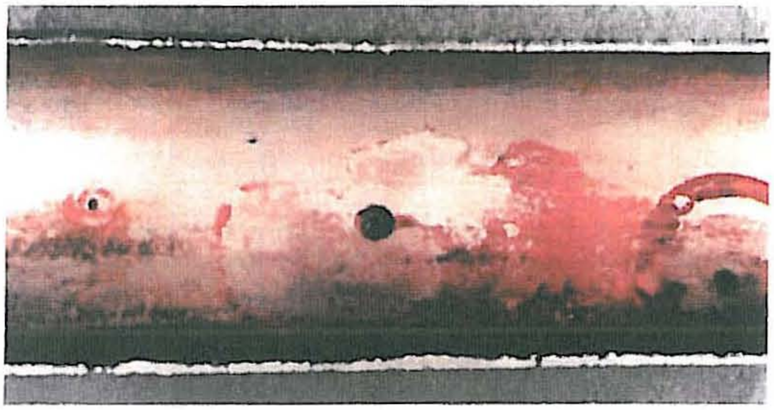


Figure 4-28.Pitting corrosion failure of an austenitic stainless steel condenser tube, due to MIC.

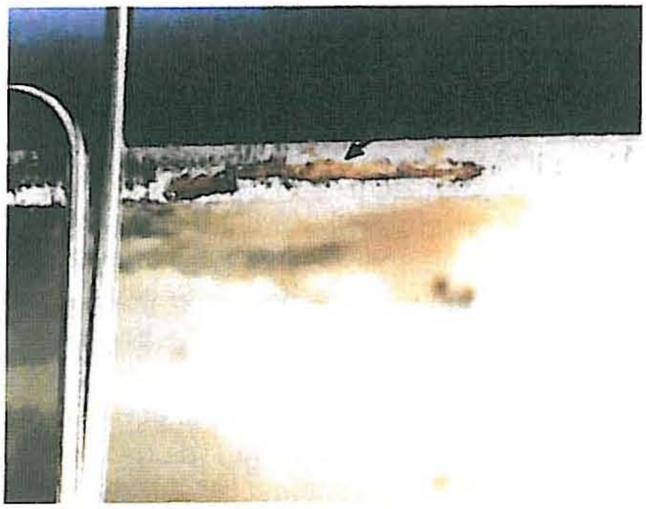


Figure 4-29. Tunneling characteristic of MIC on austenitic stainless steels. Magnification 3.5X, paper clip for size comparison.

SRBs have the capability to reduce chromates and precipitate zinc salts, and destroy chlorine. SRBs generate slime or other deposits. The most common forms are Desulfovibrio, Clostridium, and Thiobacillus.

The primary step in the reduction of sulfate to sulfide is:

$$SO_4^{=} + 8H^0 \rightarrow H_2S + 2H_2O + 2OH^- \qquad (4\text{-}38)$$

This reaction represents cathodic polarization through hydrogenase enzyme by Desulfovibrio. The net corrosion reaction is:

$$4Fe + SO_4^{=} + 4H_2O \rightarrow FeS + 3Fe(OH)_2 + 2OH^- \qquad (4\text{-}39)$$

It is important to remember that under-deposit pitting is not the only form of MIC. Bacteria and other organisms can be involved in almost every form of corrosion in cooling water systems. See section 9.4.8 on biofilms, below, for more on this subject.

### 9.4.5 Sulfuric Acid Producing Bacteria (Sulfur Bacteria)

Sulfur bacteria have the ability to convert hydrogen sulfide to oxidized sulfur compounds, including sulfuric acid. The low pH created by the acid corrodes most metals, primarily low carbon steel. Sulfur bacteria live with other organisms, primarily SRBs. Both organisms are able to draw energy from a synergistic sulfur cycle. The most common form is Thiobacillus. The sulfide oxidation reaction proceeds overall as follows:

$$2H_2O + 2CO_2 + H_2S \xrightarrow{light} 2(CH_2O) + H_2SO_4 \qquad (4\text{-}40)$$

Clearly, this light-catalyzed reaction is the opposite of the anaerobic sulfate reduction in equation (4-2) and (4-38)

### 9.4.6 Iron Bacteria

Iron bacteria are organisms that have the ability to oxidize soluble ferrous iron ($Fe^{+2}$) to insoluble ferric iron ($Fe^{+3}$) and utilize the energy of the conversion.

These bacteria are often aggressively aerobic. They scavenge the available oxygen in their microenvironment, eliminating competitive aerobic microorganisms in the microflora and readily becoming the dominant species. The soluble iron available in the water is utilized in their metabolism. As a result, their metabolic by-products include precipitated iron compounds that can accumulate to the extent that fouling problems can occur.

In some cases when no soluble iron is available in the water, the bacteria are able to excrete enzymes that attack the metal surfaces on which the colony is growing. This initiates an anodic corrosion site and subsequent MIC.

The common iron bacteria, which include Gallionella, Sphaerotilus, Crenothrix, and Leptothrix become involved with plugging and fouling problems. The filamentous colonization characteristics act as entraining and binding agents for accumulations of suspended solids and non-microbiological debris, forming troublesome deposits. These deposits not only cause fouling, but because of the oxygen scavenging capabilities of the iron bacteria within the deposit, they create a barrier that prevents the diffusion of oxygen from the water to the metal surface on which the deposit is formed. The end result is the establishment of an oxygen concentration gradient, and subsequent under-deposit corrosion.

These bacteria do not initiate corrosion, but they cause it to continue more rapidly by removing the soluble ferrous iron corrosion product from the water. They are more commonly found in once-through and potable water systems. Well waters are sometimes red with ferric hydroxide because of iron bacteria.

Because of the iron hydrolysis reactions explained in chapter 1, iron bacteria tend to concentrate chlorides, with the result that the deposits are rich in ferric and manganic chlorides. To maintain electrical neutrality, an equal number of hydrogen ions must be present to match the chloride, so that the solution beneath the bacterial deposits acts like dilute hydrochloric acid. This causes general corrosion of steel, as explained in section 5.0 and chapter 1. On stainless steels, the effect is more catastrophic, with rapid, subsurface pit cavities. Iron bacteria are aerobic, although they prefer limited oxygen supply.

### 9.4.7 Nitrifying and Denitrifying Bacteria

Nitrifying bacteria are aerobic organisms that have the ability to oxidize ammonia ($NH_3$) to nitrate ($NO_3^-$). This is accompanied by a sharp decrease in pH, as nitric acid is formed in the reaction:

$$NH_3 + 2O_2 \rightarrow HNO_3 + H_2O \qquad (4\text{-}41)$$

In one case, a sudden growth of nitrifying bacteria in an ammonia plant cooling tower caused the circulating water pH to drop from 8.5 to 3 in roughly a day, before the problem was discovered.

Nitrifying bacteria will also oxidize nitrite to nitrate:

$$NO_2^- + \tfrac{1}{2} O_2 \rightarrow NO_3^- \qquad (4\text{-}42)$$

Nitrobacter and Nitrocystis will oxidize nitrite to nitrate. Reversing these reactions, denitrifying bacteria will convert nitrite to nitrogen under anaerobic conditions.

$$2HNO_2 = N_2 + O_2 + 2OH^- \qquad (4\text{-}43)$$

Denitrifying bacteria can also reduce nitrite to ammonia instead of nitrogen:

$$2HNO_2 + 4H^+ \rightarrow 2NH_3 + 2O_2 \qquad (4\text{-}44)$$

Equations (4-41) through (4-44) are not electrochemically balanced (chapter 1), because energy is liberated and consumed by bacteria instead of by chemical reactions.

Common denitrifying bacteria include but are not limited to: Alcaligenes, Paracoccus, Acinetobacker, Aquaspirullum, and Pseudomonas. Nitrifying and denitrifying bacteria can be serious problems in closed systems using nitrite as a corrosion inhibitor (section 5). If the system is tightly sealed and anaerobic, bacterial action will cause nitrite levels to drop with no increase in nitrate. If the system has air inleakage or uses makeup water, then bacterial action will consume nitrite and generate nitrate. Thus, if nitrite is lost from a closed system, an analysis for nitrate will help in explaining the problem.

### 9.4.8 Biofilm

This section discusses attachment of bacteria to metal surfaces in cooling tower systems, to create microbiological deposits called biofilms. Biofilm formation occurs in a series of steps:

a. Bacteria arrive in the cooling water through the air and makeup water, and by reproduction in the system. The first step in biofilm formation is attachment of aerobic bacteria to surfaces. This occurs very quickly. Experiments have shown that a clean corrosion coupon exposed to a typical cooling water system collects a monolayer of organic matter and bacteria in just a few minutes.

b. If the environment is hospitable, the bacteria multiply rapidly, and other organic matter becomes absorbed in the film.

c. The cells send out hair-like exopolymers to feed on organic matter. Buildup occurs, adding to the film. The film becomes thick enough to feel and may be visible.

d. Finally, flowing water detaches some of the film, producing a dynamic equilibrium between the film and the water, and distributing the film throughout the system. The film may develop a "rippled" surface that can interfere with water flow in pipes and heat exchanger tubes.

e. Once steady state conditions are established, anaerobic conditions can develop beneath the film, at the metal surface, through the consumption and depletion of oxygen by aerobic organisms. In this way, an oxygen-free environment is created adjacent to the metal surface, making the system ripe for growth of anaerobic, corrosion-inducing organisms (MIC, section 5).

f. While the film is still "young" and very thin, other suspended solids from the water can collect at the surface and become attached. The biofilm serves as a "glue" to hold suspended matter in place. Thus, transferred corrosion products and miscellaneous dirt can become part of the growing film, and MIC can become active beneath the film.

g. Also, if the metal is a heat transfer surface, and therefore comfortably warm for bacteria, mineral scales such as calcium carbonate and calcium phosphate can form. Again, the biofilm acts as a binding agent. Theory says that the firm, attachment of mineral scales to heat transfer tubes is the result of biofilm.

## 9.5 CONTROLLING MICROBIOLOGICAL GROWTH

Controlling microbiological growth in cooling water systems is an ongoing process that must be carried out on two fronts:

- Keeping the system clean and deposit-free.
- Judiciously using microbiocides and dispersants to kill organisms and remove deposits and biofilms.

Actual procedures and choices of biocides are site-specific and depend upon water quality, opportunities for contamination and facility operations.

### 9.5.1 Tower Cleaning

The first approach must always be to keep the system as clean as possible. Deposits harbor bacteria, serve as growth sites, collect other deposits and become sites for under-deposit corrosion. Deposits also adsorb and react with biocides of all types, creating a large demand for biocides and reducing their effectiveness.

Cooling tower operators should be encouraged to schedule regular cleanings of tower basins and decks. Swab decks and basins with a dilute bleach solution if possible. If not, brush away deposits and circulate a 1-2 mg/L dose of bleach solution for an hour or two after brushing.

Monthly cleaning is good unless deposit formation requires more frequent cleaning. It is much easier and less costly to do this simple cleaning on a regular basis than it is to carry out a massive draindown and sterilization of a badly fouled tower.

### 9.5.2 Oxidizing and Nonoxidizing Biocides

Microbiocides fall into two broad groups:

Oxidizing biocides kill bacteria by destroying cells. Membranes are blocked so that the cells cannot metabolize. The more powerful oxidants actually break down (lyse) cell walls. Some less powerful oxidants can penetrate cell walls and oxidize internal cell structure. Chlorine and sodium hypochlorite (bleach solution) are by far the most widely used oxidizing biocides, followed by bromine compounds and other oxidants.

Oxidizing biocides can be applied as a continuous low-level dosage or as intermittent slug doses. Best results are usually obtained with low-level continuous dosages of 0.1 to 0.3 mg/L, plus, if needed, occasional higher slugs up to 1-2 mg/L for cleaning. Because of the reactivity of oxidizing biocides, residuals do not last long, so that to maintain a residual dosage, continuous feed is needed.

Nonoxidizing biocides do not destroy cells. Rather, they are absorbed through cell membranes into the cell, where they interfere with metabolic processes, mostly enzyme production. For this reason, nonoxidizing biocides are sometimes called metabolic biocides. A wide variety of organic compounds are used as microbiocides, including quaternary amines, sulfur compounds, aldehydes, nitrogen ring compounds (triazines) and others.

Nonoxidizing biocides are more expensive than oxidizing biocides, and larger dosages are required. However, because reactivity is lower, high dosages can be used to provide a residual that will often last for days.

Because of their toxicity, all biocides are registered with the U.S. Environmental Protection Agency and also with various state agencies. Dosages are specified on the label and special training and certification is required for operators who feed biocides to cooling systems.

Tables 4-9 and 4-10 contain lists of oxidizing and nonoxidizing biocides that are commonly used in cooling tower systems. All of these biocides and others are discussed in more detail later in this section.

**Table 4-9**
**Common Oxidizing Biocides**

| | * EFFECTIVENESS AGAINST: | | | |
|---|---|---|---|---|
| MICROBIOCIDE | BACTERIA | FUNGI | ALGAE | COMMENTS |
| Chlorine | E | S | S | Reacts with -$NH_2$ groups; effective at neutral pH; may be less effective at high pH. Use concentration: 0.1 to 0.2 mg/L continuous free residual; 0.5 to 1.0 mg/L intermittent free residual. |
| Chlorine dioxide ($ClO_2$) | E | G | G | pH insensitive; can be used in presence of -$NH_2$ groups. Use concentration: 0.1 to 1.0 mg/L intermittent free residual. |
| Bromine | E | S | S | Substitute for $Cl_2$; effective over broad pH range. Use concentration: 0.05 to 0.1 mg/L continuous free residual; 0.2 to 0.4 mg/L intermittent free residual. |
| Ozone | E | G | G | Effective over broad pH range, continuous or intermittent feed of .2 to .5 mg/L |

* E = Excellent G = Good S = Slight

### Table 4-10

### COMMON NON-OXIDIZING BIOCIDES

| | * EFFECTIVENESS AGAINST: | | | |
|---|---|---|---|---|
| **MICROBIOCIDE** | **BACTERIA** | **FUNGI** | **ALGAE** | **COMMENTS** |
| Organic bromine compounds (DBNPA) | E | S | S | pH range 6 to 8.5. Use concentration: 0.5 to 24 mg/L, intermittent feed |
| Methylenebis-thiocyanate (MBT) | E | S | S | Hydrolyzes above pH 8. Use concentration: 1.5 to 8 mg/ L, intermittent feed |
| Isothiazoline | E | G | G | pH insensitive; deactivated by -HS and -$NH_2$ groups. Use concentration: 0.9 to 13 mg/L, intermittent feed |
| Quaternary ammonium salts | E | G | G | Tendency to foam; surface active; ineffective in highly oil or organic-fouled systems. Use concentration: 8 to 35 mg/L, intermittent feed |
| Organic-tin/ quaternary ammonium salts | E | G | E | Tendency to foam; functions best in alkaline pH. Use concentration: 7 to 50 mg/L, intermittent feed. |
| Glutaraldehyde | E | E | G | Deactivated by -$NH_2$ groups; effective over broad pH range. Use concentration: 10 to 75 mg/L, intermittent feed |
| Carbamates | E | E | G | Broad spectrum activity; pH range 5 to 9. Good in high suspended solids systems; not compatible with chromate treatment programs. Use concentration: 15 to 100 mg/L |
| Dodecylguanidine (DGH) | E | E | G | Broad spectrum activity; pH range 6 to 9. Use concentration 25 to 100 mg/L |
| Triazines | NA | NA | E | Specific for algal control; must be used with other biocides. pH range 6 to 9. Use concentration: 2 to 7 mg/L |

* E = Excellent G = Good S = Slight NA = Not Applicable

### 9.5.3 Biocide Demand

One important reason for regular tower cleanings is to maximize the effectiveness of biocides. Oxidizing biocides will react with many other materials in the cooling tower besides bacteria. Other organic chemicals, oxidizable inorganic chemicals such as ferrous iron, other reactive chemicals such as amines, suspended dirt and clay, etc. all will react with oxidizing biocides.

Nonoxidizing biocides also react with substances other than bacteria. These are mostly polar organic molecules that have an affinity for surfaces. They adsorb readily on suspended solids, so that the amount available for free circulation in the water is reduced.

These concepts can be quantified in terms of "demand". The demand for any biocide in a specific system is the amount, in mg/L, that must be added to the system water before a measurable free residual can be maintained in the system. With oxidizing biocides, the demand is easily measured by laboratory amperometric titration to the first appearance of a stable free residual. In field situations, where a quick demand number is needed to estimate required dosages, for example, DPD tests can be used for a rough demand estimate.

Measuring the demand for nonoxidizing biocides is harder, because analytical methods are not available for all biocides. Nonoxidizing biocides are usually dosed based on system volume, and if possible, the measured residual is compared with calculated values. If tests are available, analytical measurements of biocide residuals vs. time are a good way to detect the presence of biofilm or other microbiological deposits in a system.

## 9.6 CHLORINE AND CHLORINE DERIVATIVES

For many years, chlorine gas was widely used as the major industrial oxidizing microbiocide. It is low in cost and very effective, but it is toxic and it presents serious safety and environmental problems. Chlorine gas has now been replaced almost completely with sodium hypochlorite and other oxidizing biocides.

Nevertheless, the chemistry and use of chlorine-based biocides can best be understood by beginning with the fundamental material, elemental chlorine.

### 9.6.1 Chlorine and Hypochlorous Acid

Chlorine gas reacts with water (hydrolyses) to form hypochlorous acid (HOCl) and hydrochloric acid (HCl).

$$Cl_2 + H_2O = HOCl + HCl \qquad (4\text{-}45)$$

Hypochlorous acid is the active biocide. Hypochlorous acid is a very weak acid (chapter 1). It dissociates in water to produce hydrogen and hypochlorite ions:

$$HOCl \leftrightarrow H^+ + OCl^- \qquad (4\text{-}46)$$

This is an equilibrium reaction that goes in both directions. Since the hydrogen ion concentration of a water solution is defined by the pH (chapter 1), the pH also determines the amount of dissociation – that is, the relative amounts of hypochlorite ion and undissociated hypochlorous acid – in the solution. In low pH (acid) solutions, the equilibrium in equation (4-46) will be forced to the left, and the hypochlorous acid will be mostly undissociated. In alkaline solutions (high pH), hydrogen ions will be neutralized and the reaction will be pulled to the left, towards hypochlorite ion.

This is very important, because as explained above, unionized hypochlorous acid is the active biocide. The hypochlorite ion has some biocidal activity, but it is roughly one-tenth as effective as the unionized acid. Thus, the efficacy of chlorine (hypochlorous acid) as a biocide is pH sensitive.

Table 4-11 below shows the availability of hypochlorous acid as a function of pH, based on the equilibrium in equation (4-46):

**Table 4-11**
**Ionization of Hypochlorous Acid**

| pH | %HOCl | %OCl$^-$ |
|---|---|---|
| 6.5 | 95 | 5 |
| 7.0 | 90 | 10 |
| 7.5 | 50 | 50 |
| 8.0 | 24 | 76 |
| 8.5 | 9 | 91 |
| 9.0 | 3 | 97 |
| 9.5 | 0 | 100 |

Table 4-11 shows that at pH 8, only 24 percent of the hypochlorous acid is available in unionized form as an active biocide. As the pH increases above 8, this percentage drops off rapidly. This explains why cooling towers operating above pH 8 require significantly more chlorine feed to maintain biological control.

However, it is not true that chlorine is not effective in alkaline solutions; it just takes a lot more to do the job. The additional chlorine impacts handling, discharge, total dissolved solids, and corrosion rates.

Chlorine and sodium hypochlorite, discussed below, react with ammonia to form a series of chloramines. The chloramines are very stable compounds that do not release chlorine easily. This can create a large demand for chlorine in systems containing ammonia contamination. Monochloramine has some biocidal activity. Municipalities sometimes add small amounts of ammonia to water to help carry chlorine residuals to the far ends of long distribution systems.

Chlorine also reacts readily with many organic molecules to form chlorinated organic compounds that create environmental problems when discharged. For this reason, large industrial plants and utility stations that discharge directly to waterways are restricted in the amount of chlorine they can use and discharge, or they may be required to dechlorinate their discharge water. This is done by adding sodium sulfite to reduce the chlorine to chloride ions.

### 9.6.2 Sodium Hypochlorite (Bleach Solution)

Commercial sodium hypochlorite solution is simply a nominal 12 percent solution of sodium hypochlorite, the sodium salt of hypochlorous acid, in excess caustic. Retail laundry bleach is the same thing, as a 3 percent solution, but the term "bleach" is also loosely used to refer to the commercial 12 percent solution.

Sodium hypochlorite solutions are unstable and gradually decompose, especially when exposed to light and high temperatures. Solutions stored in warm places may lose as much as half their activity in approximately six months. Old solutions should therefore be tested before use to determine their activity.

When added to water, sodium hypochlorite ionizes to produce hypochlorite ions, and some of the hypochlorite will react with water to produce hypochlorous acid. All of these equilibria are controlled by the pH of the solution, as explained above:

$$NaOCl \;=\; Na^+ + OCl^- \qquad (4\text{-}47)$$

$$OCl^- + H_2O \leftrightarrow HOCl + OH^- \qquad (4\text{-}48)$$

### 9.6.3 Calcium Hypochlorite [$Ca(OCl)_2$]

Calcium hypochlorite is a solid compound. It dissolves in water to produce hypochlorous acid and calcium hydroxide:

$$Ca(OCl)_2 + 2H_2O \rightarrow 2HOCl + Ca(OH)_2 \qquad (4\text{-}49)$$

The hypochlorous acid ionizes as explained above.

Calcium hypochlorite is not commonly used as a biocide except in small cooling towers. Care should be taken that calcium hypochlorite is completely dissolved and not collecting on the bottom of the tower basin. The high chlorine levels in such deposits can cause severe corrosion damage.

### 9.6.4 Isocyanurates

Chlorinated isocyanuric acid is an organic compound that slowly releases hypochlorous acid when dissolved in water. It is used as a chlorine donor in swimming pools and in both commercial and industrial cooling towers. It is supplied as the sodium salt in tablet form, and some water treatment companies also supply a liquid version.

Sodium dichloroisocyanurate contains two chlorine atoms, which are released sequentially. One molecule of sodium dichloroisocyanurate delivers two molecules of hypochlorous acid and isocyanuric acid. Isocyanuric acid helps to stabilize the hypochlorous acid from decomposition by ultraviolet radiation from the sun.

As with chlorine, the hypochlorous acid generated from dichloroisocyanurate equilibrates with hypochlorite ions as a function of pH.

### 9.6.5 Chlorine Dioxide

Chlorine dioxide is widely used as a bleaching agent in the papermaking industry, and as a microbiocide in large industrial cooling towers and municipal systems. Chlorine dioxide is an unstable gas that must be generated on site and used immediately. For water treatment purposes, chlorine dioxide is normally generated from the reaction of sodium chlorite with sodium hypochlorite and hydrochloric acid:

$$NaOCl + HCl + 2NaClO_2 = 2ClO_2 + 2NaCl + NaOH \qquad (4\text{-}50)$$

This reaction involves handling hazardous chemicals, and the generated chlorine dioxide must be carefully controlled. For these reasons, chlorine dioxide has not been considered safe for use in small industrial and commercial systems. However, other methods have been developed that do make chlorine dioxide available safely for small systems:

- Stabilized chlorine dioxide: These are simply solutions of sodium chlorite, sometimes with added caustic. When these solutions are mixed with hydrochloric acid in a tank, the chlorite ion slowly reacts with the acid to produce chlorine dioxide in solution. About 50 to 75 percent conversion can be obtained over about one hour reaction time, and the chlorine dioxide solution can then be diluted into a cooling water sidestream for use. Batch generation in this way is convenient for preparing chlorine dioxide for one-time use as a sterilizing or cleaning agent, but it is not cost-effective for continuing on-line use of chlorine dioxide as a microbiocide.
- Electrochemical generation: Sodium chlorite can be electrochemically oxidized to chlorine dioxide in a flow-through cell. This is a convenient way to prepare chlorine dioxide as needed for on-line use. Conversion is about 75 percent complete, so that the product solution contains about 25 percent unreacted sodium chlorite. The method is simple and safe, but the cells require frequent replacement.
- Dilute solutions: The standard chemical reaction (equation 4-50) can be modified for safe handling by using dilute solutions and premixing reactants. Proprietary solutions and equipment for doing this permit generating low levels of chlorine dioxide instantly as needed, with 100 percent conversion. This method should become readily available for use as interest in chlorine dioxide increases.

Chlorine dioxide is a powerful oxidizing agent, but it is more selective than chlorine. Chlorine dioxide does not react with many organic species, so that the system demand is usually lower than for chlorine. It does not form chlorinated organic compounds. Chlorine dioxide does not react with water, as does chlorine. Therefore, the biocidal effectiveness of chlorine dioxide is independent of pH – an important advantage in treating alkaline cooling systems. Finally, unlike chlorine, chlorine dioxide does not react with ammonia to form chloramines.

## 9.7 BROMINE AND BROMINE DERIVATIVES

### 9.7.1 Bromine Reactions in Water

Bromine reacts with water just like chlorine, and hypobromous acid is the active biocide. There are, however, important differences:

- Hypobromous acid (HOBr) is much less stable than hypochlorous acid. Sodium hypobromite cannot be stored and shipped commercially.
- Bromine is a weaker oxidizing agent than chlorine, but it is equally or more effective as a biocide. Because HOBr reacts less readily than HOCl, it appears to have better ability to penetrate biofilms and slimes.
- Bromine reacts with ammonia, as does chlorine, but the resulting bromamines are unstable and readily release bromine to solution. Therefore the bromamines are biocidally as effective as hypobromous acid, and ammonia in solution dos not create a "demand" for bromine.
- HOBr is a weaker acid than HOCl. Therefore it does not ionize as readily. Whereas only 24 percent of HOCl remains unionized at pH 8 (Table 4-11), 83 percent of bromine remains unionized (Table 4-12). This means that bromine, as HOBr, is a more effective biocide in alkaline cooling water systems.

**Table 4-12**

**Ionization of Hypobromous Acid**

| PH | %HOBr | %OBr$^-$ |
|---|---|---|
| 6.5 | 100 | 0 |
| 7.0 | 100 | 0 |
| 7.5 | 94 | 6 |
| 8.0 | 83 | 17 |
| 8.5 | 60 | 40 |
| 9.0 | 33 | 67 |
| 9.5 | 11 | 89 |

Figure 4-30 compares the ionization of HOBr and HOCl vs. pH, using the data from tables 4-11 and 4-12. From this graph, it is easy to see that HOBr ionizes at much higher pH levels than does HOCl. Since the unionized acids provide most of the microbiological activity, this explains why HOBr is a more active biocide in cooling water systems operating above pH 8. There are also microbiological kill data indicating that even at equal molar concentrations of HOBr and HOCl, and at the same pH, HOBr is a more efficient microbiocide.

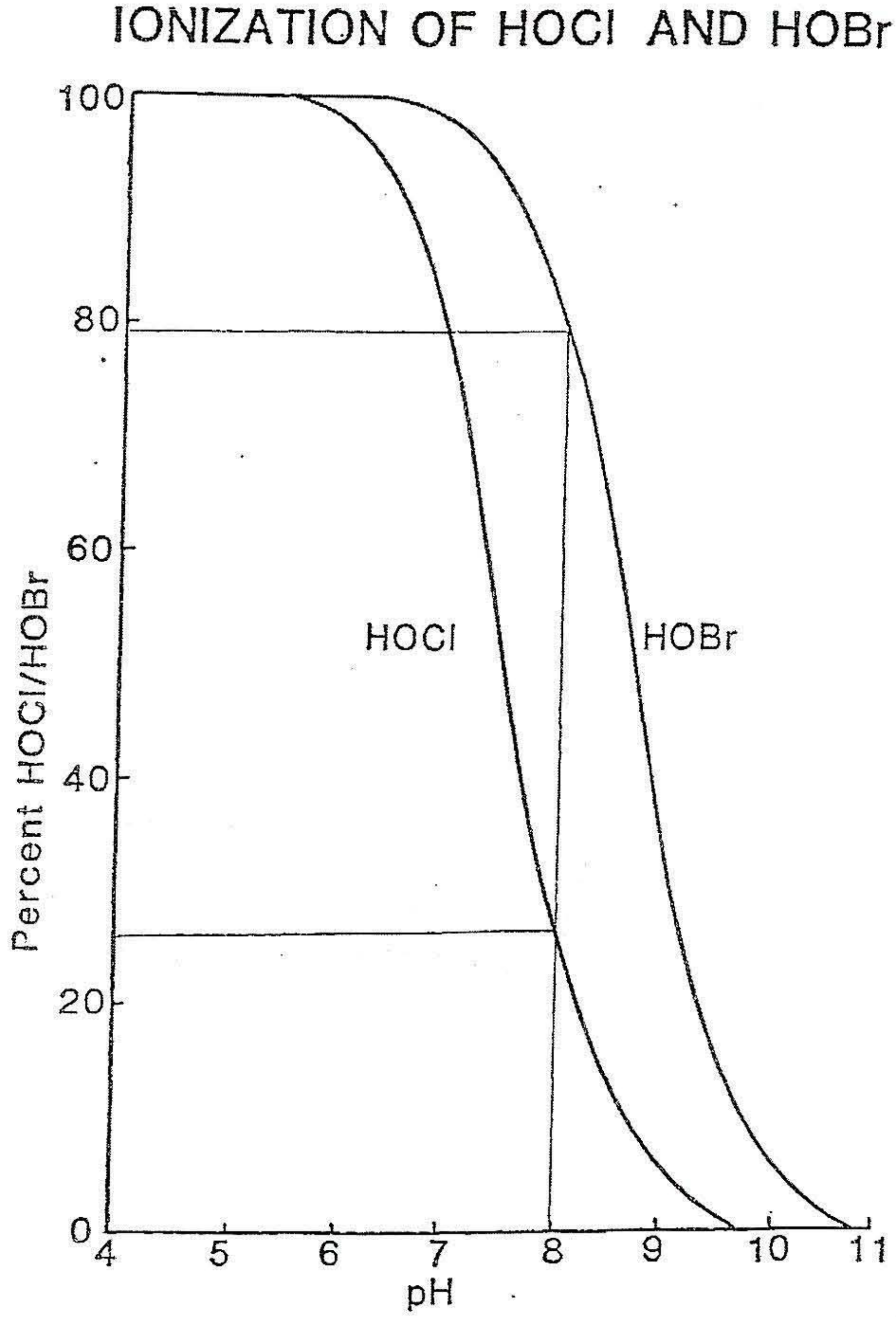


Figure 4-30. Effect of pH on ionization of hypochlorous and hypobromous acids.

Figure 4-30. Effect of pH on Ionization of hypochlorous and hypobromous acids.

9.7.2 <u>Sodium Bromide</u>

Sodium bromide (NaBr) is an inorganic salt that is readily soluble in water. Sodium bromide is not a biocide, but it reacts with sodium hypochlorite to produce hypobromous acid.

$$NaOCl + NaBr = NaOBr + NaCl \qquad (51)$$

This is a dual-feed approach. Solutions of sodium hypochlorite and sodium bromide are mixed in a reaction chamber where the reaction goes to completion very quickly, and the mixture is then pumped into the cooling system.

The concentrations of the two reacting solutions, and the pumping ratios, can be set to produce either a mixture of HOCl and HOBr or complete conversion to HOBr. The molecular weight of NaOCl is 74.5, and the molecular weight of NaBr is 103 (chapter 1). The ratio is 1:1.3. If the two solutions are pumped together in this ratio of active components, conversion will be complete. About 10 percent excess sodium hypochlorite should be used to ensure complete reaction.

### 9.7.3 Bromochlorodimethyl Hydantoin (BCDMH)

BCDMH is a white to off-white solid. It is sparingly soluble in water. BCDMH reacts with water to eventually release equal moles of HOBr and HOCl:

$$BCDMH + H_2O = HOBr + HOCl + DMH \qquad (52)$$

In practice, BCDMH pellets are placed in a bromine feeder, where they slowly dissolve or erode as water flows through the feeder. Water flow can be controlled by a timer or by an ORP (oxidation-reduction potential) controller for maintaining a continuous residual.

### 9.7.4 Liquid Bromine Products

Hypobromous acid can be stabilized by reacting it with sulfamic acid to produce a stable complex compound. The same end product can be made starting with bromine chloride (BrCl), a reaction product of bromine and chlorine. “Stabilized bromine” solutions prepared by these methods are widely used in cooling water applications.

These products are simple to pump and control, an advantage over BCDMH and NaBr + NaOCl. The disadvantage is that because the liquid is stabilized, it does not release active HOBr quickly. HOBr is released gradually, so that it is difficult to maintain a free oxidizing residual with these products. As with any oxidizing biocide, microbiological control is not reliable unless a free oxidizing residual can be maintained in the water.

## 9.8 OTHER OXIDIZING MICROBIOCIDES

### 9.8.1 Ozone

Ozone ($O_3$) is an unstable gas that readily converts to oxygen. Therefore it must be generated on-site for immediate use. The most common generation method is electrical corona discharge. Dry air or oxygen is passed through a high voltage electrical field to produce ozone. The conversion is low, about 4.5% using air or 12% using oxygen.

$$3O_2 = 2O_3 + \text{heat} \tag{4-53}$$

Ozone is partially soluble in water. It is the most powerful of the oxidizing biocides used in cooling water. Ozone degrades as a function of pH, being unstable at pH 6 and instantly degrading at pH 10. Degradation produces hydroxyl radicals ($OH^{\cdot}$), which are even more powerful oxidizers than ozone. Note: Hydroxyl radicals ($OH^{\cdot}$) are not the same as the familiar hydroxide ion ($OH^-$). Effective dosages can be as low as 0.02 to 0.05 mg/L, but the feed rate should be at least 0.1 mg/L to help account for losses and demand.

The half-life of ozone is cooling towers is very short, typically 5 to 20 minutes, because of its reactive nature and volatility. It is therefore almost impossible to maintain a free ozone residual in the water.

### 9.8.2 Hydrogen peroxide

Hydrogen peroxide ($H_2O_2$) is not a common biocide in cooling water. In-situ generation of peroxide can be achieved with peracetic acid ($CH_3COOOH$). This acid reacts in water to produce acetic acid ($CH_3COOH$) and hydrogen peroxide. Hydrogen peroxide can be used very effectively on a batch basis to remove biofilm and slime in seriously fouled systems.

### 9.8.3 Iodine

Iodine is a halogen, like bromine and chlorine, with similar chemistry. Iodine is a solid at room temperature, but with a considerable vapor pressure. It is normally handled in solutions. Iodine is useful as a medical antiseptic, and it has seen limited use as a packaged biocide for small cooling systems.

## 9.9 NON-OXIDIZING BIOCIDES

### 9.9.1 Glutaraldehyde

Glutaraldehyde disrupts the organism by cross-linking cell protein. It is effective against bacteria, yeast, and molds and most effective over a pH range of 6 to 9. Above pH 9, glutaraldehyde degrades, but can achieve rapid kill before degradation. The feed concentrations is 25 to 100 mg/L active. It is effective against both aerobic and anaerobic microorganisms.

Glutaraldehyde is deactivated by reacting with ammonia. Degradation of nitrite by denitrifying bacteria can produce ammonia. Therefore, although glutaraldehyde is frequently recommended for use in closed systems, it may be deactivated if nitrite in the system has been reduced to ammonia by microbiological action.

### 9.9.2 Isothiazolone

Isothiazolone inhibits macromolecular synthesis. It is effective against algae and sessile bacteria. It is also effective against anaerobic bacteria (sulfate reducing bacteria, SRB).

Isothiazoline is used in a pH range of 6 to 9, with pH 8 being optimum. Typical use concentrations are 1 to 5 mg/L active. The rate of hydrolysis increases with pH.

Isothiazolone is very effective against nitrifying and denitrifying bacteria.

### 9.9.3 Methylenebisthiocyanate

Methylenebisthiocyanate blocks the transfer of electrons in the respiratory system of microorganisms. It is very effective against bacteria, fungi and algae. At pH levels above 7.5, methylenebisthiocyanate hydrolyzes, but can be used effectively up to pH 8.5. The half-life of the biocide is 4 hours at pH 8.5. Typical use concentrations are 1 to 8 mg/L active.

### 9.9.4 DBNPA

DBNPA (2,2-dibromo-3-nitriloproprionamide) interacts with enzymes and interferes with cell respiration and metabolism. It is very effective against bacteria and achieves a significant kill in 1 to 3 hours. DBNPA is effective against both aerobic and anaerobic bacteria. At pH levels above 7.5, the compound hydrolyzes but can be effective up to a pH of 8.3 or higher. Typical use concentrations are 0.5 to 10 mg/L active.

### 9.9.5 Dodecylguanidine Hydrochloride (DGH)

Dodecylguanidine hydrochloride interacts with enzymes and interferes with cell respiration and metabolism. It decomposes rapidly at pH 9.5. DGH is strongly cationic and may react with anionic dispersants in cooling water treatment programs. It is effective against SRB. DGH is not a common biocide for closed systems. Typical use concentrations are 25 to 50 mg/L active.

### 9.9.6 Potassium Dimethyldithiocarbamate

Carbamates have been used for many years as effective biocides. Carbamates lose activity in alkaline solutions, particularly above pH 8.5. They have the ability to chelate metal ions that are essential elements for microbiological growth. Because of their strong chelating ability, carbamates will attack copper unless the alloy is protected by an azole. Carbamates also have the ability to precipitate iron. They are often used to remove heavy metals in waste treatment plants. Carbamates are not common as biocides for closed systems because of their instability at high pH. Typical use concentrations are 20 to 50 mg/L active.

### 9.9.7 DTEA

DTEA (2-decylthioethanamine) is one of the few new biocides to come on the market in recent years. It was designed to operate effectively under a wide range of pH levels (pH 6 to10 or greater), but especially the higher pH's now found with high alkalinity inhibitor programs. It was designed as a specific sessile bactericide, biofilm remover and biofilm growth control agent. DTEA works by forming reversible chelant complexes with the salts and inorganic ions found in biofilm structures, which severely weakens the biofilm and reduces its adhesiveness. DTEA is highly surface active. Application rates are typically 50 to 100 mg/L.

### 9.9.8 TBTO

Bis(tributyltin) oxide is a very useful algaecide and fungicide. It tends to act as a bacteriastat, rather than a bacteriacide. TBTO is deactivated by low pH, high silt, and organic fibers such as adsorption on wood fibers from a cooling tower. TBTO has been applied directly to wood cooling towers as a fungicide. The optimum pH range is 7.0 to 8.5. Solubility problems with TBTO can sometimes be encountered in the cooling system.. Feed rate is typically 40 to 100 mg/L. TBTO is less widely used today, due to risk of persistent environmental toxicity.

### 9.9.9 THPS (TKHPS)

Tetrakish(hydroxymethyl)phosphonium sulfate is promoted as one of the newest biocides on the U.S. market. It is a broad-spectrum biocide, possessing an excellent safety and environmental discharge profile. THPS functions in both open and closed cooling system over a broad pH range. It has proved useful against SRBs. THPS has limited activity in heavily fouled systems against the removal of algal biomass and biofilm slimes, and thus, its suitability as a heavy-duty biocide is questionable. THPS is cationic and if used at high concentrations there is a risk of incompatibility with anionic components of a chemical treatment program (such as polyacrylates, polymaleic acid). Feed rate is typically 60 to 80 mg/L as a 25% active material.

## 9.10 LEGIONELLA BACTERIA

Pathogenic bacteria have not been mentioned in this section because they are not normally a problem in cooling tower systems, even those using sewage effluent as makeup. Legionella bacteria are an exception to this rule, and they are discussed separately here.

AWT has published an outstanding state-of-the-art document describing the incidence and control of legionella bacteria in cooling water and domestic plumbing systems. That document should be considered the primary AWT legionella reference. The discussion in this manual is intended as a general informational survey, and is not intended to take the place of the AWT document.

### 9.10.1 Background and Incidence of Legionnaire's Disease

Legionnaire's disease is a form of pneumonia associated with a specific strain of bacteria, called *Legionella pneumophilia*, serotype 1. This is just one of over 35 species of *Legionella* that have been identified, and it is the most likely to cause serious illness. The disease is difficult to contract. It is transmitted only by inhalation of a spray or mist containing the bacteria, and it affects mostly elderly people and people with compromised immune systems. It has been fatal in about 25 percent of reported cases.

Legionella bacteria are ubiquitous and hardy. They exist in soil and are easily spread by wind currents. The bacteria exist as spores that do not grow or require nutrients, until they reach a hospitable environment. At that point they become active, reproduce and can cause infection.

Three locations where legionella bacteria can thrive, and that are important for water treatment personnel are: cooling tower basins; domestic hot water systems; and decorative fountains.

Legionella bacteria grow between about 68 and 122°F, with optimum conditions between 95 and 115°F. Does that sound like a cooling tower basin? It also sounds like a decorative fountain on a summer day and the shower heads in a hot water system. Obviously, the cooling tower and fountain waters have plenty of nutrients and dissolved oxygen, and most municipal supplies are capable of supporting this level of microbiological growth.

### 9.10.2 Cooling Towers

The first line of defense against legionella bacteria – and of course all other microorganisms as well – is proactive work to keep the system clean. Cleaning a cooling tower basin requires time and effort, and is not a pleasant job. Management needs to understand that the effort involved in routine on-line cleaning is a small fraction of what will be required for a complete draindown and sterilization if an outbreak should occur.

Monthly cleaning. Cooling tower basins should be cleaned monthly on-line, or more frequently if significant deposits develop. Procedures are obviously site-specific. Following are some suggestions that can be developed to meet specific needs:

- Sometimes one tower cell at a time can be isolated. If this is possible, drain the cell, hose down the walls and vacuum out deposits (never wash basin deposits into the sump.
- If the basin walls are accessible, brush them with a dilute solution of bleach – the exact concentration is not important.
- If the walls are not accessible, brush any parts that can be reached, and refill the basin.
- If individual cells can not be drained, simply brush the accessible walls and vacuum deposits

- When all cells have been treated in this way, raise the oxidant level in the water to 1-2 mg/L free halogen (FAH). Bleach is fine for this purpose.
- Addition of a biodispersant helps in penetrating biofilms and slimes. Hold for several hours and then allow the residual to decay.

Sidestream filters are a major benefit in helping to remove fine suspended particles that can harbor bacteria. Ideally, every cooling tower should have a filter. Obviously this is not possible, but the advantages of a filter should be evaluated for each system.

Chemical treatment should be kept up to date, standards should be high and performance should be expected. For best overall microbiological control, the target maximum total aerobic counts should be $10^4$ CFU/mL, with no visible microbiological deposits. This may be difficult to accomplish in some systems, and higher levels can be considered. However, a lot of experience says that with sufficient dedication by both operators and water treatment personnel, $10^4$ CFU/mL can be achieved. The payoff, of course, is smooth, trouble-free operations and clean systems.

Combinations of oxidizing and nonoxidizing biocides have been shown to give the best control of both legionella and general bacteria. One very good program includes 0.1-0.2 mg/L continuous free halogen residual from either bromine or chlorine, plus weekly slugs of glutaraldehyde at label dosages. "Glut" maybe used more frequently if needed.

Sterilization. Cooling towers should be sterilized (thoroughly cleaned) at the beginning of each cooling season, and again if total legionella CFU/mL exceed 100 (see testing protocol below). Sterilization procedures are very site-specific, but should include the following steps:

With the tower on-line, add bleach solution to a minimum of 5 mg/L free halogen (FAH). Circulate 6-12 hours, then drain the tower.

Physically scrub the tower basin and all accessible wetted parts. Rinse and vacuum out solids. Pressure wash the fill if possible. The intent is to remove as much deposited material as possible.

Refill and again circulate 5 mg/L FAH for 6-12 hours. Add normal chemical treatment at twice the maintenance dosage, and return to normal operation.

Testing. The controversy over whether or not to test cooling towers for legionella bacteria will continue indefinitely. The pendulum is swinging, however, in favor of routine proactive testing. The British government, for example, requires by law that every open cooling system be tested monthly.

Routine testing is certainly better than isolated spot testing. It is better than no testing because it provides ongoing information about the condition of the system and a basis for recognizing a change if it occurs. Also, a background of testing data and established cleaning procedures are evidence of the owner's good faith in working to keep his systems clean.

Testing should always be done by an independent, experienced laboratory that will take responsibility for the work and that has a background of test data against which to compare the results. Three competent laboratories are:

PathCon Laboratories, Inc. Norcross, GA

Dr. Watson, Inc. Lagrange Park, IL

Dr. Janet Stout, Pittsburgh, PA

Response to test results. This is another controversial subject. There are no standards except the British Standard, which is very severe and, in the opinion of some experts, unreasonable. The response to test results must be agreed with each facility. Remember, however, that it is much better, and easier, to do simple cleaning when counts are low than it is to suddenly find high counts and have to shut down for sterilization.

Following is a response to test protocol that is being adopted by a large group of commercial buildings in New York City:

| CFU/mL | Response |
|---|---|
| <1 | No response needed. |
| >1 <10 | Repeat test. If data confirmed, on-line cleaning, retest |
| >10 <100 | On-line clean, retest. If result lower, repeat until clean. If result higher, sterilize system. |
| >100 | Sterilize system and retest. Repeat until clean. |

### 9.10.3 Decorative Fountains

Decorative fountains can be treated much like cooling tower basins. Since there is much more public exposure with fountains than with cooling towers, it is even more important to keep the fountain basins clean. However, fountains are usually kept clean for aesthetic reasons Clean fountains should not have legionella problems.

Monthly legionella bacteria testing in decorative fountains is a good idea, but some may feel that it is overkill. This is a judgment call in each case.

However, response to positive test results should be more severe than in cooling towers because of the public exposure. Any positive test greater than 1 CFU/mL should require at least cleaning the basin of the fountain and retesting.

Chemical testing of decorative fountains is restricted to products approved by the EPA for that application. Quaternary amines have been shown to be effective in controlling legionella bacteria.

### 9.10.4 Domestic Hot Water Systems

Shower heads and drinking fountains are obvious locations where spray inhalation is possible. Shock chlorination of the water is possible, but usually a difficult procedure. Control therefore depends upon keeping the system clean, routine testing and thermal treatment as needed to kill bacteria.

Most buildings have procedures in place for cleaning their domestic water storage tanks, but this job may be neglected. This tank must be clean. If the walls are slimy, efforts to clean the hot water system will be wasted because it will be immediately reinfected.

Maintaining hot water temperature at 140°F will not permit legionella bacteria to grow. However, this is too hot for safe use of the water, and most buildings prefer lower temperatures. Occasional thermal treatment, either proactively or in response to positive test results, is therefore the best option.

Legionella bacteria are killed instantly at 170°F, and in one hour at 150°F. Thermal treatment requires that the building be empty or that all hot water faucets be secured. Heat the hot water supply tanks to at least 170°F. Circulate water and open taps on each floor, a few at a time. Let water flow until the temperature reaches 170°F, assuming little heat loss in the circulating loop. When all taps have been heated this way, the system should be clean.

Sometimes, mechanical problems will not permit heating the water to 170°F. In that case, use lower temperatures and longer times: 150°F for 1 hour, for example.

## 10.0 Cooling Water System Operations

### 10.1 SYSTEM SURVEYS AND PROGRAM SELECTION

The general subject of system surveys is discussed in chapter 1 in this manual. This section covers survey information specific to cooling water systems.

This entire chapter on cooling water has emphasized the importance of understanding each specific system to be treated. No two systems are alike, no matter how similar they may seem to be at first look. For example, two manufacturing plants, making the same products and using the same water supply, might be assumed to have similar cooling water systems. This is not necessarily so. The heat exchangers in one plant may have been designed to provide proper process cooling at a good water flow rate, while in the second plant the heat exchanges were overdesigned, either for future capacity or to provide a fouling allowance. In this plant, the operators will control process temperature by throttling heat exchanger water flow, often to very low levels. These heat exchangers become critical units that are likely to force plant shutdowns unless they are monitored and treated carefully as explained in sections 7.1 and 8.3.

As another example, consider two twin tower office buildings, constructed at the same time. These buildings may appear to be identical from the outside, but inside they may be very different. One may contain a central chiller plant, with short, large diameter condenser water piping and a large, complex chilled water system. The other may have a small chiller plant serving only public spaces, plus long risers that supply condenser water to individual tenant cooling systems on many floors. Chemical treatment programs may be similar in these two buildings, but requirements for monitoring and control of flow rates and system cleanliness will be much greater in the second building.

#### 10.1.1 General Rules For System Surveys

- Know the details of each specific system to be treated. Identify critical heat exchangers and operating procedures that will control the choice of treatment programs and monitoring methods.
- Know the history of the system. When taking over an account from a competitor, do not assume that you can just walk in and take over the systems. Find out why your competitor lost the account. If there are design and/or operating problems, insist that they be solved and work with the owner to develop a specific plan and timetable.
- Do not assume that present operating procedures are the best, or that they cannot be changed. Start from scratch and identify the problems that must be solved. Remember that chemical treatment should be the last step in the program to cost-effectively manage a cooling water system. If you do

not help the facility solve its mechanical and operating problems and improve plant efficiency, it is likely that some other vendor will.

### 10.1.2 Rules for Program Selection

There is always more than one way to treat a cooling water system, and in most cases, several different programs may be feasible. Following are general guidelines:

- Identify specific problems as described above, and build the treatment program accordingly. In most cases, the makeup water quality and plant metallurgy will be the controlling factors. For example, in a high-rise building using soft city water makeup, corrosion control on steel pipe and copper tubes may be the first requirements. However, in a utility plant using the same water but with stainless steel condenser tubes, lined water boxes and concrete piping, corrosion may not be a problem
- Do not simply repeat a previous program because that is what the facility knows, or asks for. Choose the most cost-effective program that will meet the needs of the system and that can be controlled and monitored within the capabilities of the facility.
- Similarly, do not accept plant operating conditions (pH, cycles, etc.) just because that is what the operators have learned. Design the best operating regime for the chemical program to be used, and train the facility to use the new procedures.
- Obvious statements such as these are necessary because they are so often ignored. Improper program selection and poor operating procedures are the two biggest reasons for chemical treatment-related failures in cooling water systems.

## 10.2 CHEMICAL CONTROL TECHNOLOGY

### 10.2.1 Control Ranges

Upper and lower control ranges should be established for each controllable chemical that is fed to the system. The lower limit should be the level below which performance will not be acceptable (with a small margin for error), and the upper limit should be the level above which excess chemical is wasted or may begin to cause other problems in the system.

Product control ranges may be based upon tests for an active component of the product, e.g. phosphate, or upon a specific inert chemical added as a tracer for dosage control. Tracers are convenient, but they have two disadvantages. First, use of a tracer depends upon the tracer not being lost by chemical or microbiological reactions, or by adsorption on solids in the system.

Second, a tracer analysis shows how much chemical was added to the system, but it does not show how much active material is present. For example, zinc added as a corrosion inhibitor can be lost by precipitation. Tests for a tracer chemical will not show this loss. It is therefore important to test actual active components on a regular basis whenever it is possible to do so.

Control ranges should also be established for operating parameters such as conductivity and pH, to show that cycles of concentration and pH level are correct. Cycles should be checked with several parameters, such as conductivity, alkalinity, calcium, and silica, to show that the water chemistry is correct and no precipitation is occurring (see section 7).

Finally, upper limits are desirable for ions such as iron and copper, that could indicate corrosion in the system. Suggested upper limits are:

| | | |
|---|---|---|
| Open systems: | Fe 0.5 mg/L | Cu 0.2 mg/L |
| Closed systems | Fe 0.2 mg/L | Cu 0.1 mg/L |

### 10.2.2 Analytical Tests

Based on the established control ranges, two types of analytical tests must be performed on a regular basis:

- Tests to show that chemicals are fed properly and active ingredients are within control ranges, as explained above.
- Tests to show that the water chemistry and operating parameters are within range. This requires analyzing the makeup and the tower water.

In full service accounts, the water treatment salesperson should perform all of these tests. In advisory accounts, where responsibility is shared between the water treatment salesperson and facility personnel, the facility should test operating parameters and chemical levels, so that adjustments can be made as needed. The water treatment salesperson should repeat all facility tests and should also perform additional tests for water chemistry and corrosion products.

### 10.2.3 Proper Use of Test Data

This subject is discussed in detail in chapter 1, section 10.0, and is emphasized again here because of its importance.

Analytical data are of no value unless they are used to track the condition and performance of the cooling system. Data that are stored in log books and service files represent wasted effort. The main purposes of testing are to show, on a continuing basis, that chemical levels are where they should be, the cooling system is operating at required cycles and pH, and there are no telltale signs of mineral scaling, corrosion or microbiological activity.

Plot trend graphs to show that control parameters are within range, to identify trends and to make corrections as needed. Graphs of iron, copper, cycles of concentration and total microbiological counts show ongoing system conditions. If problems occur in the system, or if undesired trends become apparent, these graphs are invaluable for identifying the source and showing when control has been reestablished.

Simple spreadsheet programs can be prepared to make data entry easy and to produce trend graphs immediately. These graphs, in addition to showing results and making problems visible, provide an incentive for all concerned to do the best job possible. Regular use of trend graphs invariably improves system performance.

## 10.3 CHEMICAL FEEDING

Methods for feeding chemicals to cooling water systems range from simple manual additions to sophisticated systems that deliver precise quantities based on system demand. Each of these systems has its place.

It is very important to choose a chemical feeding and control system that meets the needs of the system and is within the capabilities of the facility personnel. Simple and inexpensive equipment that meets the needs of small cooling water systems may not provide the degree of dosage and cost control required in large systems. Conversely, precise, elaborate and expensive control technology may be overkill for many systems, both large and small.

### 10.3.1 Manual Chemical Feed

Manual addition of chemicals is acceptable in small systems that do not have severe operating conditions and that operate consistently – that is, without sudden changes that require chemical additions or a change in dosage. The rule is to feed high levels of chemicals, so that the minimum remaining before the next application is still within guidelines. Variability is obviously high and chemicals are overdosed, so that this approach is practical only in small systems where total usage of chemicals is small.

### 10.3.2 Timer Control of Chemical Feed

Chemical pumps can be controlled by a timer set to deliver single doses of chemicals to the system at any desired frequency. This is the method of choice for feeding nonoxidizing biocides (chapter 9) and other chemicals, such as antifoams, that must be fed regularly on a slug basis, but do not require a continuous residual in the system. Timer control is not acceptable for any chemicals, such as corrosion and mineral scale inhibitors, that must be maintained at ongoing minimal levels in the system.

### 10.3.3 Chemical Feed Based on Blowdown (Bleed and Feed Method)

This is the simplest method of automated chemical feed. A conductivity controller operates a solenoid valve on the cooling tower blowdown line. The controller is preset at a level representing the desired cycles of concentration. When the solenoid valve opens to bleed the system, the controller also turns on the chemical pump, so that chemical lost via blowdown is automatically replaced. The pump stroke is set so that the chemical concentration in the system remains approximately constant.

This system is simple, reliable and inexpensive. It is certainly the most widely used chemical feeding method, especially in full service accounts and most small systems. On the negative side, the "bleed and feed" method Is not precise. It tends to produce fluctuating chemical levels that may swing above and below control ranges. Also, since the system responds only to blowdown to trigger chemical feed, it does not respond easily to situations in which blowdown frequency may be reduced, for example during low load periods. In such situations, chemicals may be consumed in the system but may not be automatically replaced.

A variation on this system is to feed chemicals as a percent of blowdown time, controlled by a solenoid valve.

As explained in sections 6 and 7, it is important not to allow chemical levels to fall below the control range, because corrosion and mineral scale protection, once lost, may not be easily reestablished. To avoid this problem with the "bleed and feed" system, dosages are set so that variations, if they occur, are more likely to be on the high side of the control range, leading to occasional overfeed.

### 10.3.4 Chemical Feed Based on Makeup (Water Meter Control)

In this system, a "pulsing head" water meter is installed in the cooling tower makeup line. The meter measure water flow and sends an electrical signal to a tower controller when a preset volume of water (e.g. 1,000 gallons) has entered the tower. The controller then signals the chemical pump(s) to deliver a present volume of chemicals. By properly calibrating the pumping time and stroke, the pumps can be set to deliver precisely the mount of chemical needed to treat all incoming makeup water. Blowdown is controlled by conductivity as in the "bleed and feed" method, but blowdown does not control the chemical pumps.

Water meter-based feed provides more precise and cost-effective control of chemical levels than does the "bleed and feed" method, with less chance for over and underfeed. This method is widely used in large commercial facilities and industrial sites. On the downside, the required equipment is more complex and expensive than "bleed and feed" equipment, while the personnel requirement to operate and maintain the system is about the same.

### 10.3.5 Other Methods For Feeding Chemicals

Some water treatment companies supply chemical pumps that are precisely calibrated to feed a specific volume of chemicals each time the pumps are activated. Other companies use direct online analyses of tracer chemicals to control the pumps. These methods do provide very precise dosage control. However, they are expensive compared to conventional chemical feed methods, and in many cases they do not offer a useful advantage. A well-maintained water meter-based chemical feed system can provide excellent control over chemical dosages within control ranges. The added control provided by special pumps or tracer analyses comes at a high price and, except in special situations, does not add useful benefit to the facility.

Further, these sophisticated systems are equipment intensive and therefore subject to failure. Facility personnel tend to assume that, having purchased elaborate equipment, they no longer have to test regularly and they do not have to maintain the equipment. Neither of these statements is true. Testing requirements, as explained in section 10.2, remain the same, and the equipment requires regular calibration and maintenance. Personnel requirements to operate these advanced systems are the same as, or greater than, for water meter-based systems.

## 10.4 CLOSED SYSTEMS

### 10.4.1 Operations

Closed systems differ from open recirculating cooling systems in two important ways. These differences have important consequences for closed cooling system operations:

- Closed system water circulates in a loop with negligible evaporation. There should be little or no makeup water required, and no blowdown, so that the circulating water does not concentrate, or cycle, as in a cooling tower system. This means that water stays in the system for long times. Chemical treatments must therefore be stable and effective for as long as necessary, without further additions of chemicals. Also, since there is theoretically no bleed-off or blowdown, there is no simple means of removing corrosion products or other suspended solids.
- Closed recirculating water systems theoretically have no exposure to air, as opposed to an open recirculating system, which depends upon aeration for cooling. Because there is no exposure to air, dissolved oxygen levels in the circulating water are very low, sometimes approaching zero. This means that corrosion inhibitors that require high levels of dissolved oxygen for performance will not be effective in closed loops. It also means that low levels of dissolved oxygen can create serious localized corrosion problems, as in boiler systems (chapter 3).

In practice, water losses and resulting makeup requirements do occur. Some common reasons for water losses from closed systems include:

- Construction or installation of new equipment, requiring complete or partial draining of the system.
- Pump seals or gland leakage. Leaking pump seals can also aspirate air into the system.

- Expansion tank overflow from surging or sudden load changes in the system.
- Leakage into or from heat exchangers and steam coils.
- Automatic or manual makeup valves leaking water into the system.
- Open or leaking drain valves.
- Over-active pressure release valves.

Closed systems may be used for process or equipment cooling (i.e. engine jacket cooling) or for comfort cooling (i.e., HVAC chilled water cooling systems). HVAC systems are discussed in section 10.4.3, below. Water velocities in closed cooling systems are generally in the 3 to 5 ft/sec range. Chilled water temperatures are usually about 40 to 50°F and the temperature rise is about 15°F.

Closed heating systems, often called hot water boiler systems, supply hot water for comfort and process heating. This term is a misnomer, since no boiling or steam generation occurs. Hot water boilers look like and operate in the same way as firetube steam generators (chapter 3). Temperatures in hot water systems range from about 120°F to 250°F in pressurized hot water systems.

### 10.4.2 Chemical Treatment

Since closed systems do not concentrate, mineral scale formation is not normally a problem, except when very hard water is used as makeup. Clean, moderately soft water is recommended as fill water for closed systems. Corrosion is therefore the major problem to be solved by chemical treatment.

Materials of construction in closed systems vary with the application. In addition to steel pipe and copper tubes, systems such as jacket water coolers and HVAC systems may contain aluminum, galvanized steel, Admiralty brass, bronze valves, various solders and sometimes other metals. Galvanic corrosion problems in closed systems are common. Pump seals and gaskets must also be protected from damage caused by suspended solids in the water and must not be attacked by the chemical treatment program.

Closed system treatment programs are unable to take advantage of the oxidizing power of dissolved oxygen and the inhibiting effect of alkalinity and hardness, as in open cooling systems (section 5). To compensate for this, closed system treatment programs operate at alkaline pH ranges from about 8.5 to 10.0, and high dosages of corrosion inhibitors such as nitrite and molybdate are used to provide protection.

In most closed systems there are many small orifices, ports, and control valves, which can be easily clogged. Suspended matter, including corrosion products and other solids, can accumulate in these orifices and restrict water flow. Closed system treatment formulations often contain dispersants (section 8) to help solids in suspension.

As pointed out above, closed cooling and heating systems sometimes do lose water, so that makeup is required. All makeup water to any closed system must be treated to ensure that chemical levels in the system are not diluted.

In some cases, due to mechanical failures or construction work, water losses become severe, so that the chemical cost to maintain residuals is high. It is tempting, under these circumstances, to reduce treatment levels. Do not ever do this. If chemical levels are maintained for more than a short time below recommended minimums, severe localized pitting corrosion may result. Once started, so that corrosion product deposits have formed, it may be difficult to arrest this corrosion without chemically cleaning the system, and this may be impossible.

When fresh makeup water enters a closed system, it often brings along microbiological contamination. Aerobic slime-forming microorganisms, anaerobic bacteria, molds, yeast, and algae can all cause problems. Bacterial slimes cause loss of heat transfer efficiency in evaporators and condensers, and in some cases can completely block the flow of water through the tubes.

Closed systems should be tested regularly for both aerobic and anaerobic planktonic bacteria. If levels greater than about $10^3$ CFU/mL are found, slug doses of a nonoxidizing biocide, such as glutaraldehyde, should be applied until counts return and hold at low levels.

### 10.4.3 Heating Ventilating and Air Conditioning (HVAC) Systems

A large majority of closed systems in commercial buildings and small industrial plants are in HVAC service. These systems have specialized design and operating requirements, that are discussed in this section.

HVAC machines (chiller machines, that manufacture chilled water for cooling) utilize one of two different designs:

- Compression units, also called mechanical chillers, using Freon as the refrigerant. Freon gas compressors may be reciprocating or centrifugal units driven by electric motors, steam turbines, or gas engines.
- Absorption refrigeration units, in which the refrigerant (water) is absorbed in concentrated lithium bromide (LiBr) solution and then evaporated by steam.

The following sections explain the operations of these two types of chiller machines in more detail.

### 10.4.4 Compression (Mechanical) Chiller Machines

The basic components of a compression chiller machine are an evaporator, a compressor, and a condenser, as shown in the center part of figure 4-31.

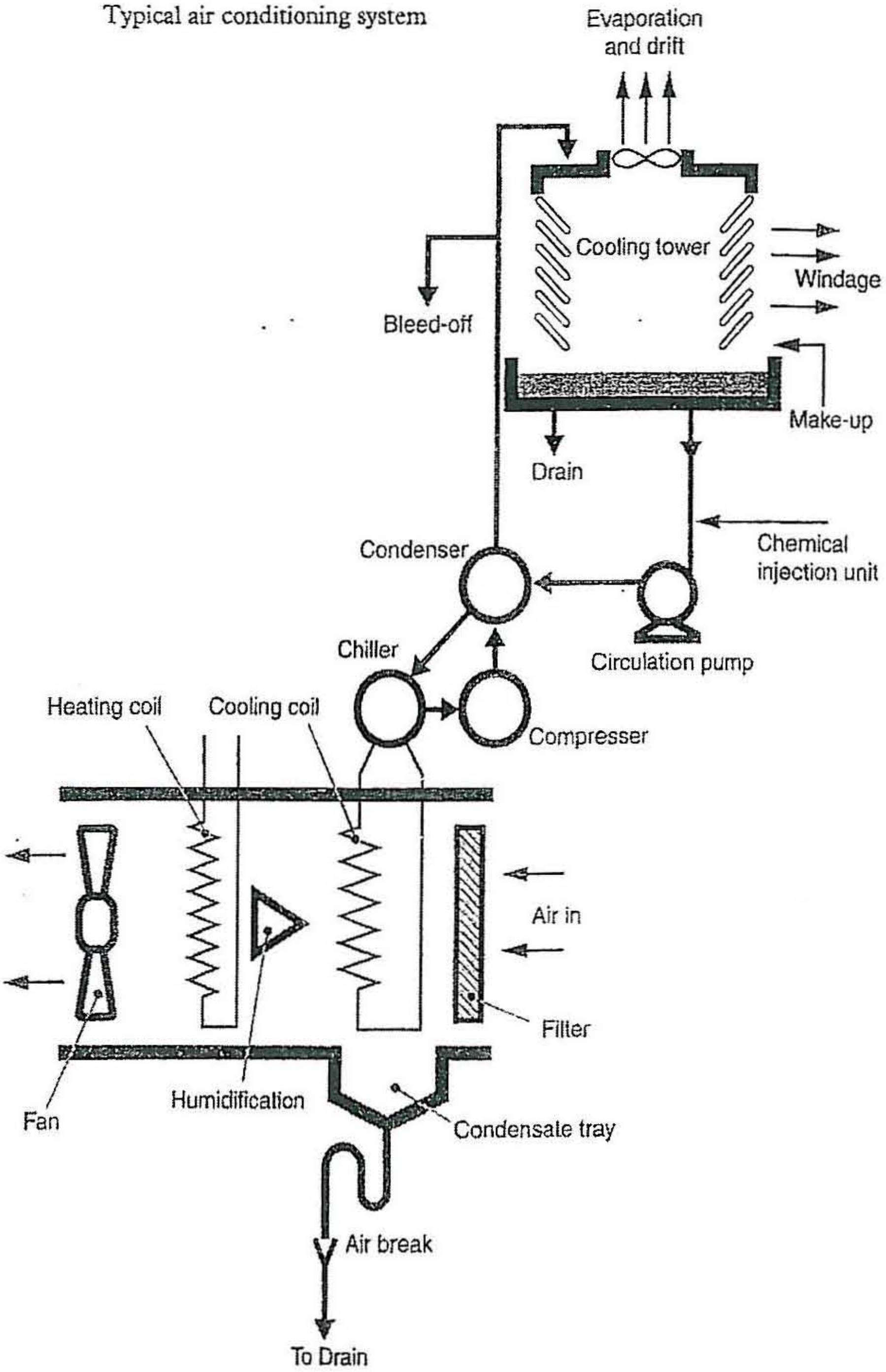


Figure 4-31. Schematic drawing of a compression chiller HVAC circuit.

The evaporator and condenser are both commonly shell-and-tube heat exchangers with water on the tube side and refrigerant (e.g. Freon®) on the shell side. Another integral part of the compression chiller circuit, not shown in figure 4-31, is the expansion valve that controls the flow of refrigerant around the circuit.

The starting point for understanding the refrigerant flow can be at any of the components, but lets start at the evaporator. Cooled low-pressure refrigerant enters the evaporator, controlled by the expansion valve, and flashes to cold low pressure liquid and vapor. The cold boiling vapor absorbs heat from a secondary source such as the closed loop chilled water circuit on the tube side of the evaporator. Chilled water may enter the evaporator tubes at 55°F and exit at 45°F.

The warmed refrigerant vapor leaves the evaporator and flows to the compressor, where its pressure and corresponding temperature are increased, and from there to the condenser section, where the hot gas is condensed into a cool, high-pressure liquid and recycled to the evaporator. Cooling tower water flowing through the tube side of the condenser removes the heat transferred from the chilled water loop plus the heat from compression of the refrigerant.

Each component in a mechanical chiller can have a variety of different designs. The evaporator section, which transfers heat from the closed chilled water loop to the boiling refrigerant, can be a shell and tube heat exchanger as described above, or a direct-expansion (DX unit) finned-tube heat exchanger. Finned-tube heat exchangers are used to chill air. The heat exchanger consists of rows of tubing through which the refrigerant flows and over which the air being cooled flows. Similarly, condenser sections can be either water or air cooled.

The expansion valve, that also can be deigned in various ways, feeds the cooled liquid refrigerant into the evaporator at the proper rate. If too much liquid refrigerant enters the evaporator, not all of the liquid refrigerant will change to a vapor. If liquid refrigerant is transported to the compressor it can damage compressor valves. If there is not enough refrigerant to absorb the heat from the returning closed loop cooling water, then the water will not be sufficiently cooled, reducing efficiency. By modulating the refrigerant flow in response to cooling demand, the valve maintains the proper amount of liquid in the evaporator.

### 10.4.5 Lithium Bromide Absorption Chiller Machines

A typical lithium bromide/water (Li Br/$H_2O$) absorption-refrigeration machine cycle includes four stages, as shown in Figure 4-32:

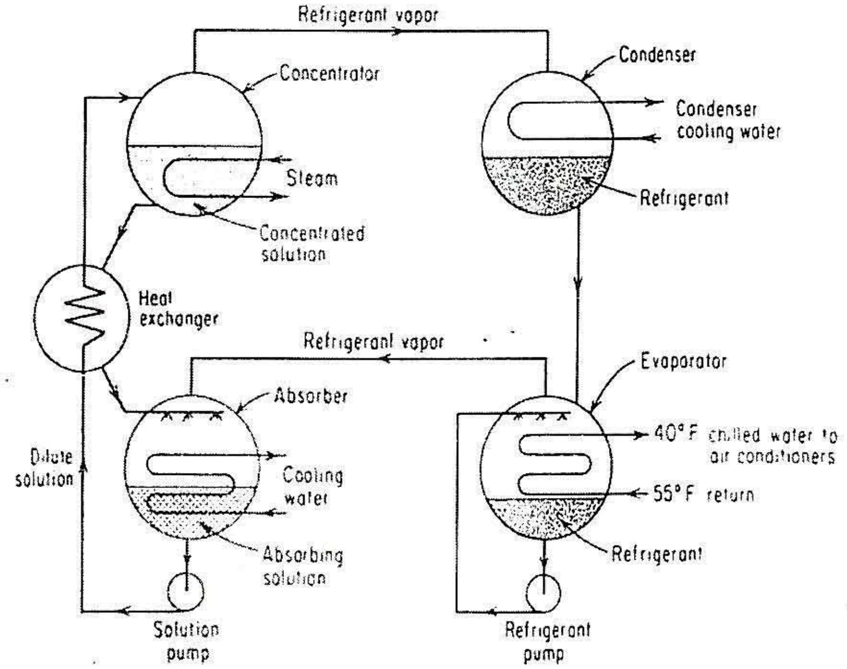


Fig 4.32: A typical adsorption refrigeration machine flow diagram

1. Generator – where steam heat generates water vapor (refrigerant liquid) from hot dilute lithium bromide solution.
2. Condenser - where hot water vapor is condensed to create liquid water by the cooling tower/condenser water system.
3. Evaporator - where liquid water evaporates under vacuum to cool the chilled water loop for used for air conditioning.
4. Absorber – where the hot water vapor (refrigerant liquid) is absorbed into the concentrated lithium bromide/water solution.

Note that the condenser and evaporator in an absorption chiller perform the same functions that they do in a mechanical chiller described above.

Typically a lithium bromide refrigeration unit consists of two horizontal shells. The shells can be placed one on top of the other, or side-by side. Normal configuration is one shell on top of the other. In this configuration the upper shell contains the generator and condenser, and the lower shell, the absorber and evaporator.

Heat, in the form of steam, is supplied in the generator section to the lithium bromide/water solution. This heat causes the refrigerant (water) to be boiled out of the solution in a distillation process. The resulting water vapor passes into the condenser section, where cooling water to the heat exchanger is used to condense the vapor back to a liquid state.

The water then flows down to the evaporator section where it passes over tubes containing the water from a closed loop to be cooled. By maintaining a very low pressure in the absorber-evaporator shell, the water boils at a very low temperature. This boiling causes the water to absorb heat from closed loop be cooled, thus, lowering its temperature.

Evaporated water then passes into the absorber section where it is mixed with a strong LiBr/$H_2O$ solution that is very low in water content. This strong LiBr solution tends to absorb the vapor from the evaporator section to form a weaker solution. This is the absorption process that gives the cycle its name. The weak solution is then pumped to the generator section to repeat the cycle.

An advantage of a lithium bromide absorption refrigeration unit is that it uses excess steam or low electrical power as the input energy source. The unit is preassembled at the factory and requires a relatively small space for installation. The refrigerant, water is non-toxic and non-hazardous.

However, the refrigeration unit operates continuously under high vacuum, and any inward leakage of air subjects the internal parts to corrosion. Under an air in-leakage condition, the concentrated lithium bromide solution (58-65 % LiBr) is susceptible to crystallization, and the refrigerant lines can freeze. The best policy for good operation of a lithium bromide absorption unit is not to break into the unit but to maintain good machine vacuum.

### 10.4.6 Chiller Efficiency

HVAC systems are one of the highest energy consumers in most facilities, and there is always a strong incentive to keep these systems running as efficiently as possible. From the water treatment side, this means keeping the cooling tower and the condenser and evaporator tubes as clean as possible.

One of the main causes of decreased chiller efficiency is tube fouling. According to one chiller manufacturer, Trane, there is approximately a 1.5 percent loss in cooling efficiency for each degree increase in condensing temperature. For example, consider a 500 ton chiller operating at 70% load, 24 hours a day, 200 days per year, at 0.6/kWh power cost and 0.9kW/ton power requirement for chiller operation. Table below shows the increase in cost as the fouling factor for the condenser tubes increases.

**Table 4-13**
**Effect of Fouling Factor on Chiller Operating Costs**

| Fouling Factor | Film Thickness On Tube (inches) | C-Factor | % Increase in Energy | Added Energy Cost/Year |
|---|---|---|---|---|
| 0.0005 | 0.006 | | 5.3 | $5,724 |
| 0.001 | 0.012 | 1170 | 10.8 | $11,664 |
| 0.002 | 0.024 | 990 | 21.5 | $23,220 |
| 0.003 | 0.036 | 830 | 32.2 | $34,776 |

The fouling factor (chapter 1, section 2.2.6) is simply the reciprocal of the heat transfer coefficient for a condenser tube.

An easily calculable parameter for monitoring condenser performance is the C-factor shown in Table 4-13. The C-factor is also called the orifice coefficient. This parameter measures only waterside fouling, and not heat transfer. This parameter is designed for fixed-size orifices where "C" is the constant for the orifice. The orifice, in this case the tube diameter opening, is a fixed size and shape. Thus:

$$\text{Flow} = C \times \text{square root of } \Delta P \qquad (4\text{-}53)$$

Unfortunately, in cooling water systems the tubes do not always stay clean, changing the C value. A back calculation for C will show if a change in orifice coefficient has occurred. The C-factor measures both tube plugging and uniform fouling. The value of C decreases as fouling occurs. When fouling occurs, the effective diameter of the tube decreases. For a given flow, the pressure drop ($\Delta P$) will increase by the fifth power of the ratio of the clean diameter to the fouled diameter.

For example: Design flow for a specific condenser is 550 gpm at a $\Delta P$ of 17 psi. Thus,

$$C_{design} = \frac{\text{Flow}}{\text{sq rt }(\Delta P)} = \frac{550}{\text{sq rt }(17)} = 133 \qquad (4\text{-}54)$$

By comparison, a fouled system having a flow of 150 gpm and a $\Delta P$ of 55 psi has a C-factor of 20, indicating the condenser is heavily fouled.

A reduction in the condenser water flow rate can be attributed to throttling back the flow, dirty strainers and filters, microbiological film, and scale and deposits on the tube surfaces. Not only will microbiological film reduce flow, but also it is the second most thermally resistant film to heat transfer.

### 10.4.7 Primary and Secondary Closed Loops

Most simple closed systems consist of a single closed cooling circuit, or loop. In a chilled water system, the chilled water absorbs heat from air in fan coils large air handling units, or process equipment, and then exchanges this heat with an open cooling system in a shell and tube heat exchanger. In a hot water system, the hot water loses heat in fan coils and other units, and is reheated in a hot water heating boiler (chapter 3).

Some high-rise commercial buildings and manufacturing plants are designed with primary and secondary closed loop systems. For example, a primary chilled water loop may service air handling units that cool public spaces in a large building, while one or more secondary loops cool tenant spaces.

Secondary closed loops exchange heat with the primary closed loop system, not with condenser water. There are two types of secondary closed loop systems:

- In plate-and-frame systems, the primary and secondary loops exchange heat in a plate-and-frame heat exchanger. The two systems are completely isolated and never mix. Therefore they must be treated independently.
- In injection systems, the temperature of the secondary loop water is controlled by periodic injections of primary chilled water into the secondary system. A corresponding amount of warmer secondary water is forced back into the primary system. The two systems are completely mixed and can be treated as one system.

It is, obviously, very important to recognize the existence of secondary closed loops when doing a system survey. Some secondary systems have been severely damaged because the vendor failed to recognize that they were plate-and-frame systems that required separate treatment.

Even injection systems may have problems that are different, and usually more severe than the primary system. For instance, in commercial buildings, the primary chilled water system may contain large diameter pipes that service only air handlers that require a substantial continuous flow of chilled water. The secondary system, on the other hand, may provide water to tenant spaces that vary widely in size and usage. Some parts of the system may contain pipe sizes one inch in diameter or less, and flow rates may be intermittent or zero during night and weekend hours.

### 10.4.8 Closed Condenser Water Systems

Open condenser water systems often contain suspended solids and biological matter scrubbed from the air in the cooling tower. To avoid this contamination in sensitive cooling applications, these systems are sometimes designed as closed loops. An open condenser water system exchanges heat through a plate-and-frame heat exchanger with a closed cooling loop. Since no chiller is involved, this loop is, in effect, closed condenser water.

Closed condenser water loops may be found in commercial buildings that house large data processing centers. The closed loop removes heat from Liebert units (small chiller machines) that cool data processing equipment. Closed condenser water systems are also found in buildings that contain many tenant-operated direct expansion (DX) cooling units that require condenser water but no chilled water. These systems represent another opportunity for serious errors in system surveys. It may be assumed that all condenser water can be treated at the cooling tower when, in fact, a closed condenser water loop exists that cannot receive any treatment from that system.

### 10.4.9 Ambient Cooling (Free Cooling) Systems

In some parts of the country, the temperature of the open condenser water system may sometimes be low enough to permit using this water directly to cool fan coils and air handling units. This bypasses the chiller machines and saves significant amounts of electric power. To make this system work, condenser water may be valved to flow through the chilled water lines. Later, when the ambient temperature increases, the system can be returned to normal operation. This leaves the chilled water system filled with condenser water.

Direct injection of cooling tower water into a "closed" chilled water loop in this way can lead to significant problems in a facility. The condenser water contains bacteria, suspended solids, and low inhibitor levels compared to normal closed loop chemical treatment. This represents poor water quality conditions for a closed loop. Corrosion rates can be high, microbiological growth can be rapid, and suspended solids can accumulate in the system.

The best way to avoid this problem is to isolate the cooling tower water from the chiller unit through a plate and frame heat exchanger. This eliminates contamination of the chilled water closed loop. The cooling tower water can be chemically treated using a variety of traditional approaches, without concern for the chilled water. A filter should always be installed between the cooling tower and the plate and frame heat exchanger, to reduce the potential for fouling the heat exchanger.

## 10.5 COOLING SYSTEM LAYUP

Improper layup of cooling systems, either for an outage or long-term storage, is a major source of damage to operating equipment. Simply turning off pumps and closing valves on an open or closed cooling system, or alternatively draining the system and leaving it empty and wet, are two sure ways to invite serious corrosion and microbiological fouling problems.

Layup procedures are site-specific, depending on unit design, system characteristics, metallurgy, length of intended layup, etc. Following are general guidelines that should be followed in all cases. These guidelines apply to both open and closed cooling systems, except as noted.

### 10.5.1 Wet Layup

Wet layup is used mostly for short-term outages, or when the unit must be returned to service on short notice.

1. Add a double or triple dose of the corrosion control program, a double dose of oxidizing biocide and an all-purpose nonoxidizing biocide, e.g. glutaraldehyde. Alternatively, a special layup product containing high levels of inhibitors may be used.

2. Circulate for 6-12 hours, then close the system. If a cooling tower is involved and the layup period is to be more than a few days, drain the system below the basin level and allow the tower to dry out.
3. Circulate the system monthly. Test the corrosion inhibitor level monthly and add chemical as needed.

### 10.5.2 Dry Layup

Dry layup is best for longer-term outages and for equipment storage when quick return to service is not expected.

1. Follow step 1 above for wet layup.
2. Circulate for 6-12 hours, then drain the system as completely as possible. Drain all dead legs and use compressed air to blow water out of low points where possible.
3. Leave the system open to allow remaining water to evaporate. Cooling tower basin drains should be covered. After a week or two, the system may be closed, but do this only if necessary.
4. On startup, add a double or triple dose of treatment chemicals as the system is filled. When the system is circulating, add a double dose of oxidizing biocide to cooling towers, and nonoxidizing biocide to both open and closed systems.

### 10.5.3 Vapor Phase Corrosion Inhibitors

Vapor phase corrosion inhibitors (VpCI) are explained in section 5.10.12. VpCI provide excellent corrosion protection and are highly recommended for use in layup programs. Some major advantages are:

In wet systems, VpCI will protect metals in any air pockets, and will protect the system if any water losses occur.

In closed systems, it is not necessary to air blow low points to remove standing water. VpCI will protect both wet and dry surfaces, including wet spots beneath deposits that might otherwise continue to corrode. Dry systems must be closed to prevent loss of inhibitor.

VpCI can simply be added to the circulating water in place of the double inhibitor dose recommended in step 1 of the procedures above. Follow the manufacturer's directions, and be sure to select the proper inhibitor product to protect all the metals in the system. Chlorine at 1-2 mg/L and other microbiocides may also be used.

### 10.5.4 Fire Protection Systems

Fire protection piping systems are not cooling water systems. However, they share many of the characteristics and problems of closed, stagnant water systems, and treatment programs are similar.

There are two basic types of fire protection systems:

1. Wet systems, in which the pipes are always filled with water under pressure held by the sprinkler heads.
2. Dry systems, in which the pipes are dry and under air pressure held by the sprinkler heads, and pressurized water is held by a control valve. Any sudden drop in air pressure opens the control valve and allows water to rush through the pipes.

Some systems may be operated wet during the summer months and dry during winter when freezing may be a problem. Dry systems, in fact, are never really dry after the first use or testing of the system.

Corrosion, particularly microbiologically influenced corrosion (MIC), is the major problem in fire protection systems. Dissolved oxygen in the water is consumed by corrosion reactions, the systems become anaerobic, and SRB and other anaerobic bacteria thrive. Pinhole leaks appear, and this is often the first indication of problems because it is very difficult to inspect these systems.

Corrosion protection in these systems has been difficult because of the danger of public exposure to the water. Vapor phase corrosion inhibitors (VCI) (section 10.5.3) solve this problem. VCIs are safe to use and effective in controlling corrosion in both wet and dry systems. The VCI must be added to the water used to fill wet systems and to test dry systems. Follow manufacturer's recommendations for product selection and packaging method. Chlorine at 1-2 mg/L may also be added to the fill water to help control microbiological growth.

## 11.0 Monitoring System Performance

Every cooling water system, large and small, should include some ongoing method of monitoring performance – that is, demonstrating that corrosion, mineral scaling, microbiological fouling and general deposition are under satisfactory control, that the system is operating at or close to design specifications, and that operating costs are acceptable.

As with chemical feeding methods (section 10.3), many different techniques are available for monitoring performance, ranging from simple analytical tests to complicated electrochemical measurements. The choice of methods must be site-specific. The monitoring program must provide useful information upon which action decisions can be made. The monitoring data must be capable of interpretation directly in terms of facility operations, and the cost of the monitoring program must be reasonable to both the water treatment company and the facility.

### 11.1 DIRECT vs. INDIRECT PERFORMANCE MONITORING

Obviously, the best method for assessing the performance of a cooling water chemical treatment program is direct inspection of the heat exchangers and system piping. Inspections are the ultimate proof of performance and the proof of reliability of other test methods. Equipment should be inspected every time it is available, and careful photographic records and written descriptions should be kept on file after each inspection.

Unfortunately, operating cooling equipment is available for inspection only when the system is shut down. On the average, this may occur once a year, or in some cases once every three to five years. Indirect methods therefore must be used to track system performance between inspections. It is always assumed that the various indirect monitoring methods discussed in this section all reflect exactly the condition of the actual system. This is a dangerous assumption at best. For many reasons that are discussed in this section, indirect monitoring tools may respond differently to system conditions. It is therefore very important to compare monitoring information with direct system inspections at every opportunity.

Some indirect measurements can be very close to direct information. Some examples are:

Heat transfer calculations on operating heat exchangers, using system temperatures and flow data, can be compared with design information. If the heat exchanger is operating close to design performance, it can be assumed that the unit is clean, at least within the design fouling allowance (chapter 1). The cooling tower approach temperature and chiller operating efficiency are two easy calculations that can be used to compare unit operations with design specifications (see section 11.4.2 in this chapter, and chapter 1). However, these calculations tell nothing about possible corrosion inside the unit.

Similarly, analytical test data can show that no mineral scales are precipitating and that no corrosion product ions are appearing in the water. These are direct system measurements, but as with heat transfer calculations, they are still one step removed from actual equipment inspections.

## 11.2 CORROSION COUPONS

Corrosion coupons are simply strips of metal, typically 0.06 x 0.5 x 3 inches in length. The coupons are preweighed, attached to nonmetallic holders to avoid galvanic effects, and installed in specially designed coupon racks in the system. After exposure, the coupons are removed, cleaned and weighed. Corrosion rates are calculated form the weight loss, and other information about the coupons is recorded.

### 11.2.1 Preparation

Coupons are made from carbon steel, copper, stainless steels and other alloys that may be present in specific cooling systems. The specific alloys used must be typical of that used in system piping and equipment. The coupon surfaces must be carefully prepared to be clean and uniform, and the freshly prepared surfaces must be protected from atmospheric corrosion before the coupons are used.

All of this work can be done in-house. However, the best way to obtain reliable coupons with uniform metallurgy and surface preparation is to purchase them from a supply house that specializes in this work. Coupons are supplied preweighed and ready to use, in protective envelopes.

### 11.2.2 Installation

As explained in section 7, corrosion rates are strongly influenced by water composition, temperature and flow rates. Coupon locations in the system must therefore be selected to provide representative information. One coupon rack should always be installed on the hot water return line to the cooling tower. In a commercial building, this may also be the high point in the system. If practical, a second rack should be installed, either at the low point or at a location that has experienced operating problems, such as reduced water flow.

The best way to install corrosion coupons is in a specially designed coupon rack. The rack provides controlled flow rate and easy installation and removal of coupons. Figure 4-33 is a schematic drawing of a corrosion coupon rack.

## TYPICAL CORROSION COUPON RACK

**All piping is mild steel (black iron)**

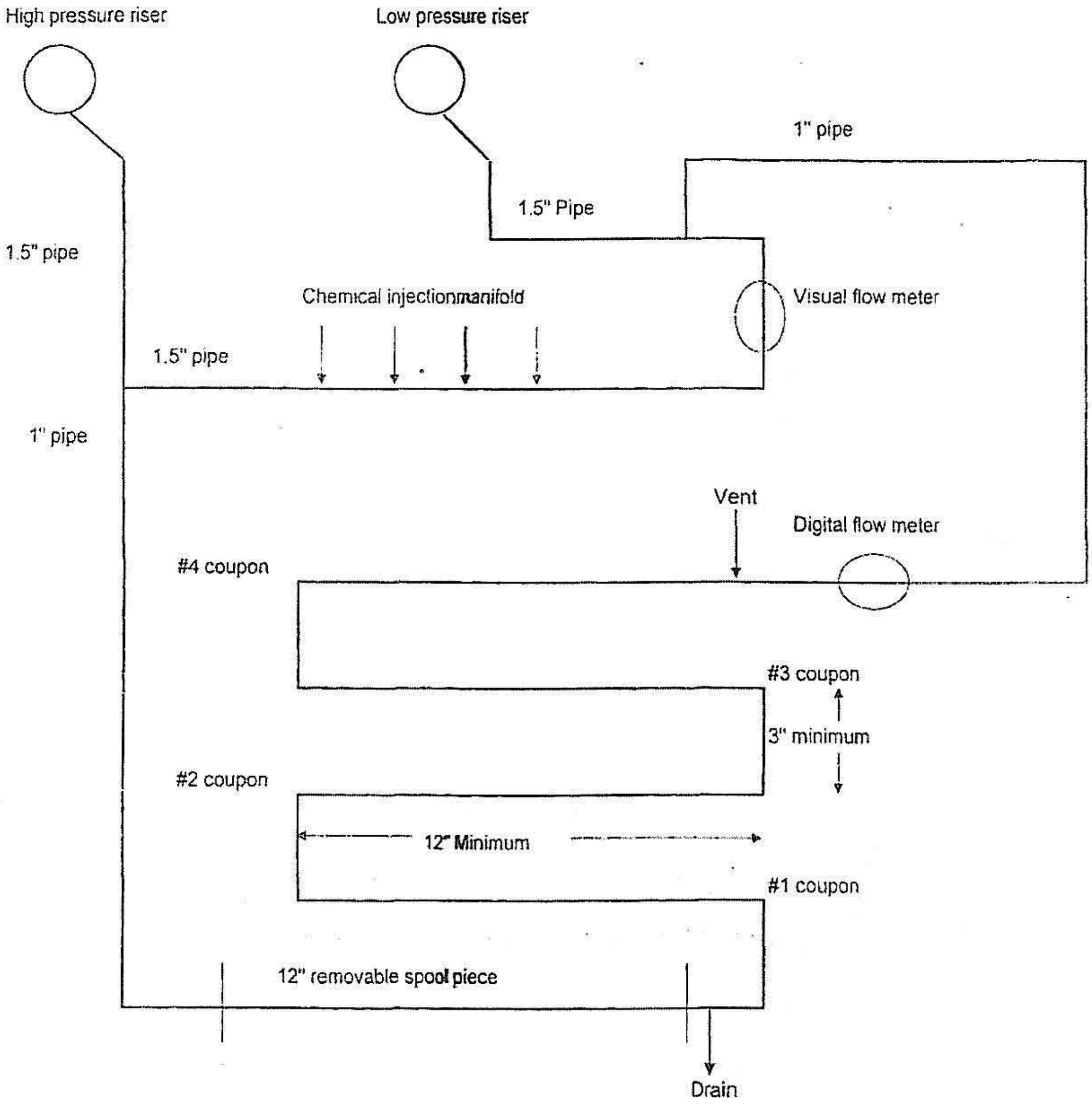


Figure 4-33. Drawing of a typical corrosion coupon rack

The rack should be made from one-inch diameter PVC or carbon steel pipe. PVC provides a clean rack and simple installation. Carbon steel, however, offers a distinct advantage: that is, the opportunity to inspect the inside pipe surfaces. These surfaces represent the actual system more closely than any prepared surface corrosion coupon. A removable spool piece can be installed with unions, that allow the spool piece to be removed periodically for inspection and then either replaced or returned to service.

The rack must contain a flow meter as shown, isolation and throttling valves, and a drain. The rack is installed in a vertical plane, with water flow from the bottom to the top of the rack. A flow rate of 8 gpm through one-inch pipe represents a velocity of 3 feet per second. As explained in section 5, this is a rough minimal velocity to help prevent settling of solids in the system. Higher or lower velocities can be used as required.

The rack must be placed so that there is sufficient pressure drop across the rack to provide the required water flow. If this pressure drop is not available, a booster pump must be used. Also, the rack must be placed upstream from all chemical feed points and on a separate bypass line.

Coupons must be installed in a vertical plane, to help prevent solids from settling on the surfaces. Coupon locations are designed so that water flows from the holder out over the coupon surface. This helps to avoid impingement problems that sometimes develop if water directly hits the exposed end of the coupon.

### 11.2.3 Exposure

As explained in section 5, corrosion rates on freshly exposed metal surfaces decrease with time, due to polarization and passivation effects. For this reason, the exposure time of coupons in the rack is a critical factor in producing useful data. For normal monitoring purposes, a 90-day exposure time is about right. Monthly (30 day) exposure should not be used except in unusual circumstances, such as when chemical cleaning is in progress or when recovery from a serious problem is being tested. Monthly coupons are also useful for studying short-term effects such as inhibitor film formation and effects of system upsets. Figure 4-34 shows corrosion coupons exposed in a well-treated building HVAC system for 25, 55 and 85 days.

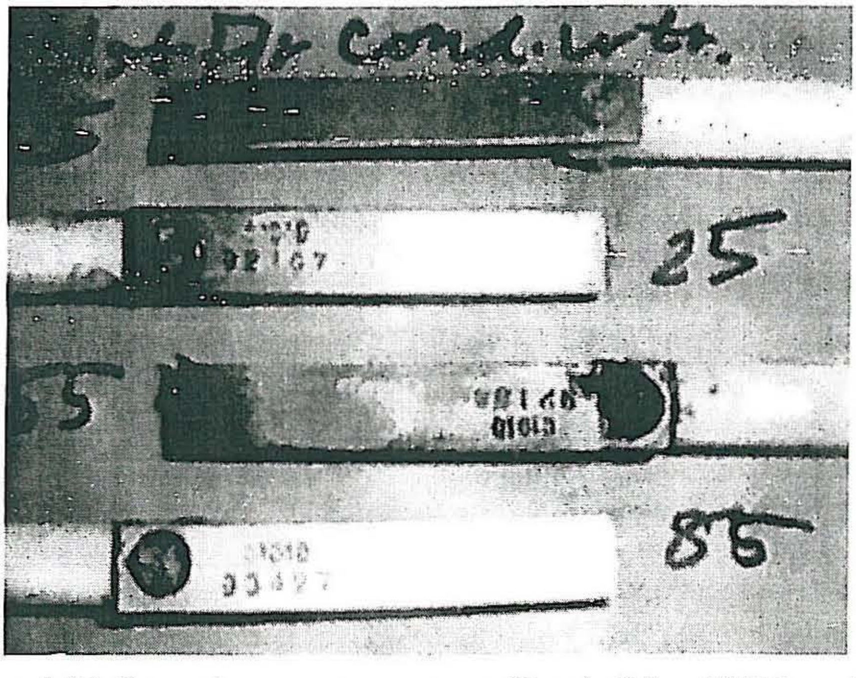


Figure 4-34. Corrosion coupons exposed in a building HVAC system.

Chemically passivated coupons are sometimes used to counteract the effects of high initial corrosion rates. This is a questionable practice. For special case short-term exposures, there may be some value in prepassivation, but such data should not be assumed to represent system conditions. Over a 90-day exposure period, experience has shown that there is no significant difference between prepassivated and fresh coupons.

### 11.2.4 Interpretation of Corrosion Coupon Data

In addition to the weight loss data, important information about system conditions can be obtained from coupon examinations. Coupons should be photographed wet as removed from the system, and the photographs should be kept on file. Progress in removing general system deposits can be documented in this way. The coupon rack should be inspected when the coupons are removed, for evidence of microbiological slime and other deposits.

Localized, under-deposit corrosion should be noted when coupons are removed, and again after they have been cleaned and weighed. If under-deposit corrosion is serious, the problem should be investigated and resolved quickly. Remember, however, that fresh, clean coupon metal surfaces are more sensitive to localized corrosion that are the aged, passivated interior pipe surfaces. Serious under-deposit corrosion on coupons should be investigated, but it does not necessarily mean that the pipe surfaces are in the same condition.

Coupon weight loss data represent average corrosion rates obtained over the exposure time. They do not show what the corrosion rate was at any specific time. In that sense, coupon corrosion rates are a good indicator of average system conditions, provided that flow rate and temperatures are reasonable and that the coupon data correlate well with system inspections.

One way to obtain more timely coupon data is to use overlapping coupons. For example, if three carbon steel coupons can be installed in a rack, one coupon can be removed every 30 days on a rotating basis. After the first 60 days, this amounts to removing a 90 day coupon every 30 days. With these data plus analytical test results, it is often possible to pinpoint when corrosion or deposition problems began.

Coupons are not heat transfer surfaces. Coupon results may be typical of internal pipe surfaces, end bells, etc., but they do not correlate well with corrosion on heat exchanger tubes.

Overall, corrosion coupons are widely used and popular. They are simple, reliable when properly installed, and inexpensive. They provide good average corrosion rates, plus indications of localized corrosion and system deposits.

## 11.3 LINEAR POLARIZATION RESISTANCE (LPR) PROBES

Electrochemical corrosion measurements use various experimental techniques to actually measure the corrosion current flowing between a corroding electrode and a reference (see chapter 1 for information on corrosion mechanisms and electrochemical reactions). Important scientific information can be gathered about corrosion processes by studying these electrochemical reactions.

These same methods can be used to estimate corrosion rates in operating systems. The most widely used electrochemical method for this purpose is called linear polarization resistance (LPR). The method involves applying a small potential (20-40 mV) across two identical electrodes made from the metal under study, and measuring the resulting current flow. The LPR instrument uses this current to calculate a corrosion rate. The instrument is small and portable, or it can be rack-mounted. Readings can be taken continuously or intermittently. LPR probes are conveniently sized to fit into corrosion coupon racks such as in Figure 4-33, so that coupon and LPR data can be obtained simultaneously and compared.

Several different commercial versions of LPR instruments are available. Some use two electrodes as shown in figure 4-35, while others use a third reference electrode. Since these instruments measure corrosion currents in water, it is necessary that the water have sufficient conductivity to carry the current. The method works well in cooling water systems, but it cannot be used, for example, in demineralized water.

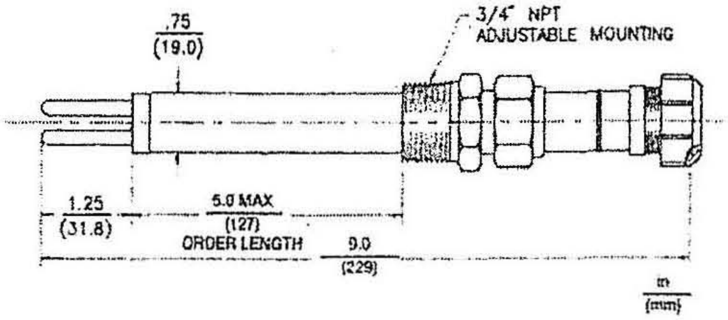


Figure 4-35. Linear polarization resistance (LPR) probes.

There are two major differences between LPR and corrosion coupon data:

- LPR rates are calculated from corrosion currents. The rates are not measured directly, as are coupon weight loss data. Many factors can influence the measured corrosion currents. LPR data are therefore so-called "second generation" data, even further removed from actual system rates than are coupon data.

- LPR data are "instantaneous", or real time data. That is, the LPR instrument measures the corrosion current and calculates a corrosion rate at the moment the measurement is taken, whereas coupon rates represent an average rate over the period of exposure.

These two differences affect the way LPR data are used and interpreted. LPR data may or may not be close to actual corrosion rates. In general, coupons and LPR probes agree within about twenty percent. The most useful aspect of LPR data is not the actual corrosion rates but the ability of the instrument to respond quickly to changes in rates.

LPR data can be plotted versus time, as shown in figure 4-36. These are typical trend graphs, similar to those used with analytical data. The ability of LPR probes to respond quickly to changes in system corrosivity represents the main value of this method. LPR control units can be automated with a simple recorder and an alarm, to warn of high corrosion rate excursions before any significant damage is done. The same thing can be accomplished with daily or even weekly manual LPR probe readings, as long as the data are plotted on a trend graph.

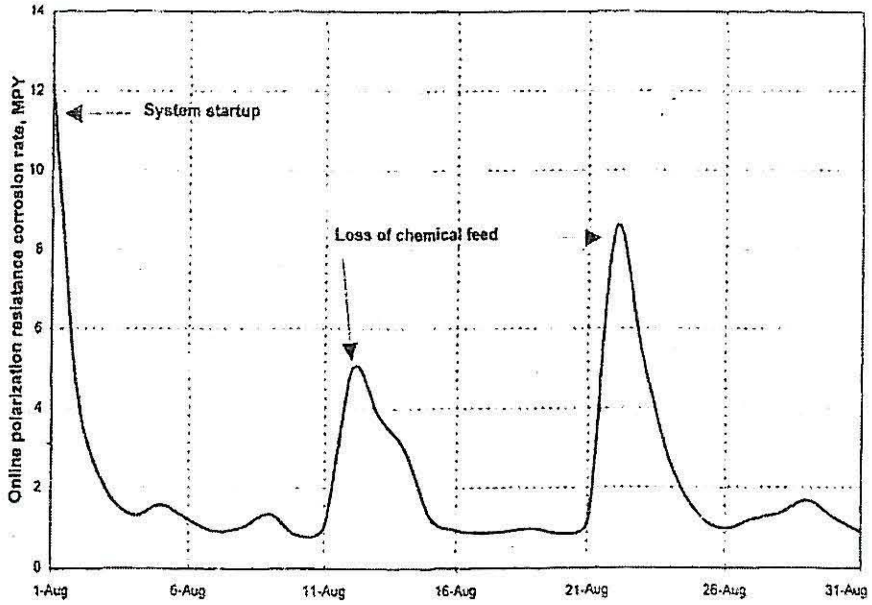


Figure 4-36. A typical LPR corrosion rate trend graph.

Because of this quick response capability, attempts have been made to use LPR to control the feed of corrosion inhibitor. This has not been successful, because other factors, in addition to inhibitor feed, can affect the corrosion rate.

LPR data have also been used to predict pitting corrosion rates. Some LPR instruments will calculate a so-called "pitting index" by comparing the difference in corrosion currents when the direction of polarization is reversed.

There is no theoretical basis for this calculation, and "pitting index" data should be ignored.

## 11.4 SCALE AND DEPOSIT MONITORING

### 11.4.1 Pilot Scale Test Heat Exchangers

Test heat exchangers are common simulation devices in cooling water systems. When properly used, these units allow measurements of fouling and corrosion under conditions that approximate field heat exchangers.

A small section of heat exchanger tubing is heated electrically to represent heat transfer conditions in an operating unit. The heated tube is installed concentrically inside another tube, usually transparent plastic, and water flows through the annular space between the two tubes. The size of the annular space and the flow conditions are adjusted to approximate hydrodynamic and thermal conditions in the operating system.

This simple test system can be assembled in many different configurations. For example, the test heat exchanger can be installed:

- On a sidestream from an operating cooling system.
- As a separate recirculating pilot unit using synthetic concentrated water.
- In a pilot cooling tower system, so that effects of makeup water quality, cycles and holding time can also be studied.

In any of these configurations, monitoring can be by simple visual observation of the heated tube. Also, thermocouples can be imbedded in the tube and the temperature data used for direct calculations of fouling factors (chapter 1). The system can be expanded to include corrosion coupons, LPR probes and microbiological test equipment.

Pilot scale test heat exchanger systems are available commercially, or they can be assembled from available parts. Figure 4-37 shows a typical commercial unit. As simple visual test heat exchangers, these systems are not expensive. In most cases, when the unit is used as a long-term on-line monitoring tool, visual inspections of the heat transfer tube will be sufficient. However, when completely instrumented for automatic data collection and included as part of a complete pilot cooling tower system, costs can be high.

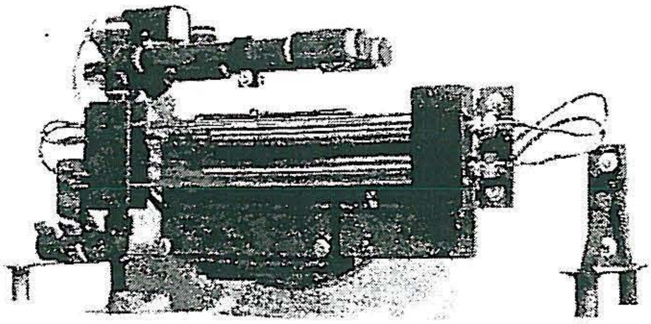


Figure 4-37. A commercial cooling water test heat exchanger

It is important to choose operating conditions for a pilot test heat exchanger carefully. The unit can be operated to simulate a specific heat exchanger, or to test the most severe conditions in the field system. If temperature and flow data are collected for fouling factor calculations, the data should be plotted on trend graphs.

### 11.4.2 Direct Monitoring of Heat Exchanger Efficiency

Cooling water and process operating data can be used to monitor the performance of field heat exchangers, using the heat transfer principles explained in chapter 1 and in section 4 of this chapter. Exact calculations of U values (heat transfer coefficients) are complex and require controls that are usually not available in operating units. However, several simple, approximate calculations can be made that, when trended over time, can show changes in heat transfer capability of the heat exchanger.

- Approach temperature and terminal difference measurements.

  1. Measure the cooling water inlet and outlet temperatures, and calculate the cooling water temperature change (CW$\Delta$T).
  2. Use a thermometer, a calibrated thermocouple, or if necessary, an infrared temperature gauge, to measure the process side outlet temperature.
  3. For a noncondensing heat exchanger, subtract the cold cooling water temperature from the process outlet temperature to obtain the approach temperature. For a refrigeration or steam condenser, subtract the cooling water outlet temperature from the hot well temperature to obtain the terminal difference temperature.
  4. Plot the CW$\Delta$T, approach temperature and terminal difference temperature on trend graphs. If these parameters trend upwards with time, waterside fouling may be occurring.

These calculations depend upon maintaining steady state operating conditions. A change in process flow, steam demand or cooling load, or a change in cooling water basin temperature, will affect the data, so that these variables should also be collected and plotted. Over time, changes in average operating conditions will become clear, above any cyclic or random changes in process operations.

- Log mean temperature difference (LMTD). The LMTD (section 4.2.3) represents the driving force for heat transfer in a countercurrent or cocurrent heat exchanger where no condensation occurs. Under steady state operating conditions, the LMTD will normally increase with time if mineral scaling or fouling occurs in the unit. As above, the LMTD will also change with process variables, so these should also be plotted.

### 11.4.3 System Inspections

System inspections are the best available way to recognize and monitor growth of mineral scales and fouling deposits in non-heat transfer portions of the cooling system. Cooling tower decks, fill and basins, coupons and coupon racks are all readily available for inspection. Dead legs should be blown down regularly, and heavy accumulations of deposits should be analyzed. Similarly, pump strainer deposits should be analyzed, especially if the amount of deposit increases with time. Sand filter backwash water is another source for collecting system deposits.

Mineral scale deposits will usually form first on heat transfer surfaces, but will also appear on hot water surfaces such as tower decks and fill. General fouling deposits will collect wherever flow rates are low enough to allow settling, or where corrosion products provide a rough surface to catch deposits.

Remember that it is much easier and less expensive to keep a system clean than it is to clean a heavily fouled system. Any change in amount or type of deposition in the system should be noted so that corrective actions can be taken before the problem becomes serious.

## 11.5 MICROBIOLOGICAL MONITORING

### 11.5.1 System Inspections

There is no substitute for regular inspections as an early warning sign of biofouling in a cooling water system. A slimy feel on tower basin walls, visible algae on the fill or deck, slime on coupons and coupon racks are all signs of biofouling. Swab samples from any of these locations can easily be cultured for microbiological activity. Microbiocide additions and, if necessary, operating routines should be changed immediately to correct these conditions (section 9), before fouling progresses far enough to affect heat transfer and/or reduce water flow.

### 11.5.2 Planktonic Biomass

Planktonic (free floating) bacteria levels in open cooling water systems should be monitored regularly using dip slides. Only aerobic bacteria can be monitored reliably in this way. Dip slides are available for anaerobic bacteria, but since open cooling systems are aerated, anaerobic bacteria counts have little meaning.

Keep in mind that aerobic bacteria, by themselves, are not usually harmful in cooling systems. They serve mainly as an indicator of potential biofilm formation, because system deposits are the main reservoir (source) for planktonic bacteria. If planktonic total counts are low, e.g. $10^3$ CFU/mL, it is likely, but not guaranteed, that there will be little or no biofilm in the system. If counts are high, e.g. $10^5$ CFU/mL, the source of the bacteria must be found and eliminated.

Dip slide data should be supported by quarterly laboratory plate counts that provide an accurate calibration point for the dip slide data. Also, serial dilution bottle tests can be performed on-site to assess bacteria levels. By using different culture media in the bottles, different species of bacteria can be encouraged to grow. This technique can be useful when testing the efficacy of different biocides in a system.

Instrumental methods are also available for testing total planktonic counts in water. The best known of these is the bioluminescence method, based on enzymes produced by fireflies, that react with biological matter to produce flashes of light. A major advantage of this technique is that data are available in a few minutes, compared to two or three days for dip slides. On the negative side, the instrumentation is expensive, and the enzymes react with all biological matter, living and dead, including both bacteria and plant material. For this reason, the luminescence method is not suitable for use in tests for microbiocide efficacy.

### 11.5.3 Sessile Biofilms

Sessile (attached) biofilms are the source of major problems in cooling water systems (section 9). As explained in section 11.4.1, physical inspections are the best monitoring tool for sessile bacteria and algae. The presence of slime on any test surface is an indication that slime is also forming in less accessible portions of the system, notably in heat exchangers.

Special techniques are also available for monitoring sessile biofilm formation:

- Pressure drop monitors. A pressure drop monitor is simply a length of small diameter pipe or tubing with a manometer or differential pressure gauge, as shown in Figure 4-38. The pipe is connected as a bypass in parallel with the cooling water system, usually on the hot return side. The change in pressure drop with time is a measure of biofilm formation in the pipe. The pipe is made from stainless steel or glass to eliminate corrosion products that can attract and hold bacteria, while at the same time providing a surface that is conducive to growth. Since no heat transfer is involved, mineral scales do not usually form in these devices, but suspended solids can be trapped in developing biofilm, especially at low flow velocities.

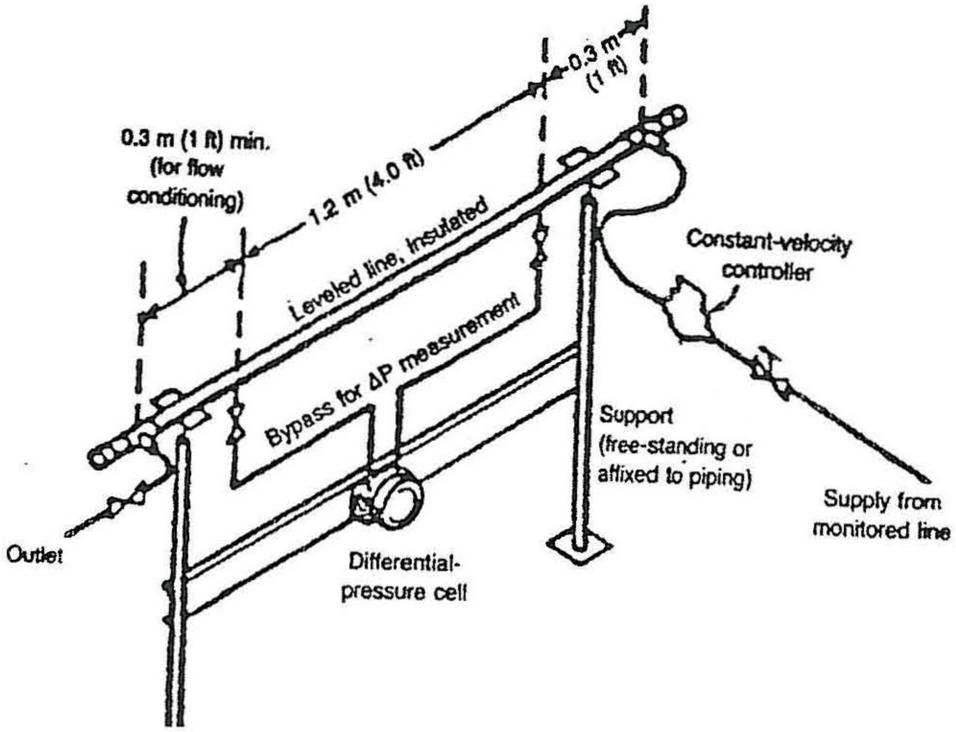


Figure 4-38. Drawing of a biofilm pressure drop monitor.

In order to make the pressure changes meaningful, flow through the test pipe must be constant. This is done by including a doie valve or other constant pressure device in the system. Pressure drop can be plotted vs. time, and deposits can be analyzed.

- Fill boxes. As explained in section 3, fouling of film-pack tower fill is a serious concern. Biofilms can easily bridge the spaces between fill sheets, thus preventing proper water flow through the tower. Once fouled, film-pack fill is very difficult to clean except by mechanical methods that often damage the fill.

  An easy way to monitor biofilm growth in tower fill is to suspend a section of fill in a box with open top and bottom, in an accessible location in the "rain" below the fill in the tower. The fill can be inspected regularly by touch, and swab samples can be cultured. Figure 4-7 is a photograph of a working fill box.

  An effective early response to growth of biofilm on film-pack fill is to inject oxidizing biocide (section 9) directly into the hot water return line to the cooling tower. Some or all of this biocide may be lost by volatilization in the tower, but the resulting clean fill is well worth the short-term use of additional chemicals.

- Other tests for sessile bacteria. Coupons made from screening mesh and installed in coupon racks are sometimes used as biofilm collection devices. Other suspended solids will also become trapped on these coupons. A column of glass beads provides a growth surface for biofilm. A small number of beads can be removed regularly for culture tests. These tests are useful, but they do not provide more information than can be learned from a regular inspection program in the operating system, as explained in section 11.4.1.

## 12.0 Glossary

Active: The negative direction of electrode potential. Also the state of a metal that is corroding without significant influence of reaction product.

Aeration cell: See Differential cell

Amphoteric metal: A metal that is susceptible to corrosion in both acid and alkaline environments.

Anaerobic: Free of air or uncombined oxygen.

Anion: A negatively charged ion that migrates through the electrolyte (water) towards the anode under the influence of a potential gradient

Anode: The electrode of an electrochemical cell at which oxidation occurs. Electrons flow away from the anode in the external circuit. Corrosion usually occurs and metal ions enter the solution at the anode.

Anodic inhibitor: A chemical substance that prevents or reduces the rate of the anodic or oxidation reaction.

Anodic polarization: the change of the metal's potential in the noble (positive) direction caused by current across the metal/electrolyte (water) interface (see Polarization).

Antifouling: Preventing fouling (see Fouling).

Aerobic: In the presence of air or combined oxygen

Austenitic steel: A steel whose microstructure at room temperature consists of predominately of austenite.

Blowdown: The process of discharging a significant portion of the aqueous solution (cooling water) to remove accumulated salts, deposits, and other impurities.

Buffer: A substance that prevents ph changes when present in the electrolyte (water).

Brittle fracture: Fracture with little or no plastic deformation.

Calcareous deposit: A layer consisting of calcium carbonate and other salts deposited on the surface. When the surface is cathodically polarized, this layer is the result of the increased pH adjacent to the surface.

Cathode: The electrode of an electrochemical cell at which reduction is the principal reaction. Electrons flow toward the cathode in the external circuit.

Cathodic corrosion: Corrosion resulting from a cathodic condition of a metal, usually caused by the reaction of an amphoteric material with the alkaline products of the electrolysis.

Cathodic inhibitor: A chemical substance that prevents or reduces the rate of the cathode or reduction reaction.

Cathodic polarization: The change of the electrode potential in the active (negative) direction caused by current across the metal/water interface (see Polarization).

Cathodic protection: A technique to reduce the corrosion of a metal surface by making the surface the cathode.

Cation: A positively charged ion that migrates through the electrolyte (water) toward the cathode under the influence of a potential gradient.

Cavitation: The formation and rapid collapse of cavities or bubbles within a liquid, which often results in damage to a material at the solid/liquid interface under conditions of severe turbulent flow.

Cell: See Electrochemical cell.

Chloride stress corrosion cracking: Cracking of a metal under the combined action of tensile stress and corrosion in the presence of chlorides and electrolyte (usually water).

Concentration cell: An electrochemical cell, the electromotive force of which is caused by a difference in concentration of some component in the electrolyte (usually water). This leads to the formation of discrete cathodic and anodic regions.

Concentration polarization: That portion of polarization of a cell produced by concentration changes resulting from passage of current through the electrolyte (usually water).

Conductivity: The capacity to conduct electricity in an electrolyte (water). Measured as micromhos/centimeter (μmho/cm) or microsiemems/centimeter (μS/cm). μS/cm is the SI –System International unit).

Contact corrosion: See Galvanic corrosion.

Corrosion: The deterioration of a material (usually a metal) that results from a reaction with its environment.

Corrosion fatigue: Fatigue-type cracking of metal caused by repeated or fluctuating stresses in a corrosive environment characterized by shorter life than would be encountered as a result of either the repeated or fluctuating stress alone or the corrosive environment alone.

Corrosion inhibitor: A chemical substance or combination of substances that, when present in the environment, prevents or reduces corrosion.

Corrosion products: The products of the corrosion reaction, which are solid or semisolid.

Corrosion potential ($E_{corr}$): The potential of a corroding surface in an electrolyte (usually water) relative to a reference electrode under open-circuit conditions. Also known a rest potential, open circuit potential, or freely corroding potential.

Corrosion rate: The rate at which corrosion proceeds.

Corrosion resistance: Ability of a material, usually a metal, to withstand corrosion in a given system.

Corrosiveness (corrosivity): The tendency of an environment to cause corrosion.

Couple: See Galvanic corrosion

Crevice corrosion: Localized corrosion of a metal surface at, or immediately adjacent to, an area that is shielded from full exposure of the environment because of closed proximity of the metal to the surface of another material.

Critical pitting potential ($E_p$, $E_{pp}$): The lowest value of oxidizing potential (voltage) at which pits nucleate and grow.

Current density: The current to or from a unit area of a surface.

Dealloying: The selective corrosion of one or more components of a solid solution alloy. Also known as selective dissolution.

Depolarization: The removal of a factor resisting the current in an electrochemical cell.

Deposit attack: Corrosion occurring under or around a discontinuous deposit on a metal surface.

Desulfovibrio: A genus of bacteria that reduces sulfate to $H_2S$ and obtains energy by oxidation of $H_2S$ or organic molecules.

Dezincification: A corrosion phenomena resulting in the selective removal of zinc from copper-zinc alloys.

Differential aeration cell: A corrosion, the electromotive force of which is due to a difference in air (oxygen) concentration at one section of the metal surface as compared with that at another section of the same material.

Diffusion-limited current density: The current density that corresponds to the maximum transfer rate that a particular species can sustain because of limitation of diffusion.

Double layer: The interface between a metal or suspended particle and an electrolyte (water) created by charge-charge interaction leading to an alignment of oppositely charged ions at the surface of the metal or particle.

Electrochemical cell: A system consisting of an anode and a cathode immersed in an electrolyte (water) so as to create an electrochemical circuit. The anode and cathode may be different metals or dissimilar areas on the same metal surface.

Electrochemical reaction: A chemical reaction characterized by a gain or loss of electrons at the metal surface.

Electrode: A conductor used to establish contact with an electrolyte (water) and through which current is transferred to or from an electrolyte.

Electrode potential: The potential of an electrode in an electrolyte (water) as measured against a reference electrode.

Electrolyte: A chemical substance (usually water), containing ions that migrate in an electric field.

Electromotive force series: A list of elements arranged according to their standard electrode potential, the sign being positive for elements whose potentials are cathodic to hydrogen and negative for those anodic to hydrogen.

Embrittlement: Loss of ductility of a material resulting from a chemical or physical change.

EMF series: See Electromotive force series.

Environment: The surrounding of conditions (physical, chemical, mechanical) in which a material exists.

Environmental cracking: Brittle fracture of a normally ductile material in which the corrosive effect of the environment is a causative factor.

Erosion: The progressive loss of a material from a solid surface due to mechanical interaction between that surface and a fluid, a muticomponent fluid, or solid particles carried with the fluid.

Erosion-corrosion: A conjoint action involving corrosion and erosion in the presence of a moving corrosive fluid or a material moving through a fluid, leading to accelerated loss of material.

Exfoliation corrosion: Localized subsurface corrosion in zones parallel to the surface that result in thin layers of uncorroded metal resembling the pages of a book.

Facultative bacteria: Bacteria that can live either in the presence or absence of oxygen.

Fatigue: The phenomenon leading to fracture of a material under repeated or fluctuating stresses having a maximum value less than the tensile strength of the material.

Ferrite: The body-centered cube crystalline phase of iron-based alloys.

Ferritic steel: A steel whose microstructure at room temperature consists predominately of ferrite.

Ferrobacteria**:** Any of a group of bacteria that oxidizes iron as a source of energy. The oxidized iron, in the form of $Fe(OH)_3$, is the deposited in the environment by secretion from the bacterium.

Fouling: An accumulation of deposits on a surface.

Fretting corrosion: Deterioration at the interface of two contacting surfaces under load, which is accelerated by their relative motion.

Fungus (fungi): Any of a major group of parasite plants that lack chlorophyll, including molds, mildew, smut, mushrooms and yeasts.

Galvanic corrosion: Accelerated corrosion of a metal because of an electrical contact with a noble metal or nonmetal conductor in a corrosive electrolyte (water).

Galvanic couple: A pair of dissimilar conductors, commonly metals, in electrical contact in an electrolyte (water).

Galvanic current: The electrical current between metals or conductive nonmetals in a galvanic couple.

Galvanic series: A list of metals and alloys arranged according to their corrosion potential in a given electrolyte (solution).

General corrosion: Corrosion that is distributed more or less uniformly over the surface of a material.

Graphic corrosion: Deterioration of gray cast iron in which the metallic constituents are selectively leached or converted to corrosion products, leaving the graphite intact.

Heat-affected zone (HAZ): That portion of the base metal that is not melted during brazing, cutting, or welding, but whose microstructure and properties are altered by the heat of these processes.

Heat treatment: Heating and cooling of a solid metal or alloy in such a way as to obtain desired properties.

High pressure cleaning: Water cleaning performed at pressures from 5,000 to 10,000 psig.

High-pressure water jetting: Water jetting at pressures from 10,000 to 25,000 psig.

Holiday: A discontinuity in a protective coating that exposes unprotected surface to the environment.

Hydrogen blistering: The formation of subsurface planer cavities, called hydrogen blisters, in a metal resulting from excessive hydrogen pressure. Growth of near surface blisters in low-strength metals usually results in surface bulges.

Hydrogen embrittlement: A loss of ductility of a metal resulting from absorption of hydrogen.

Hydrogen-induced cracking: Stepwise internal cracks that connect adjacent hydrogen blisters on different planes in the metal, or to the metal surface.

Hydrogen stress cracking: Cracks that result from the presence of hydrogen in a metal in combination with tensile stress. Occurs most frequently with high-strength alloys.

Impingement corrosion: A form of erosion corrosion generally associated with the local impingement of a high-velocity, flowing fluid against a solid surface.

Intergranular corrosion: Preferential corrosion at or along the grain boundries of a metal.

Intergranular stress corrosion cracking: Stress corrosion cracking in which the cracks occur along grain boundaries.

Ion: An electrically charged atom or group of atoms.

Iron bacteria: See Ferrobacteria.

Langelier index: A calculated saturation index for calcium carbonate that is useful in predicting scaling behavior of waters.

Liquid metal cracking: Cracking of a metal caused by contact with a liquid metal.

Low-carbon steel: Steel having less than 0.3% carbon and on intentional alloying elements

Low-pressure water cleaning: Water cleaning performed at pressures less that 5,000 psig.

Martensite: A hard supersaturated solid solution of carbon in iron characterized by an acicular (needle-like) microstructure.

Microbiocide: Any chemical that will kill microorganism. Used synonymously with biocide and bactericide.

Microbiologically-influenced corrosion (MIC): Corrosion resulting from the growth of microorganism that have created an environment for corrosion process to exist by forming an oxygen-barrier deposit on a metal surface or by producing metabolic by-products, such as organic/inorganic acids that attack metal surfaces.

Microorganism: Any organism of microscopic size that requires a microscope to be seen.

Mill scale: The oxide layer formed during hot fabrication or heat treatment of metals.

Noble: The positive direction of electrode potential, thus resembling noble metals such as gold and platinum.

Noble metal: A metal that occurs commonly in nature in the free state.

Noble potential: A potential more cathodic (positive) than the standard hydrogen potential.

Oxidation: Loss of electrons by a constituent of a chemical reaction.

Oxidation-reduction potential (Redox potential): The potential of a reversible oxidation-reduction electrode measured with respect to a reference electrode.

Oxygen concentration cell: See Differential Aeration Cell.

Passivation: A reduction of the anodic reaction rate (corrosion rate) of the metal involved in corrosion.

Passive: A state of a metal in which a surface reaction product causes a marked decrease in the corrosion rate relative to that in the absence of the product.

Passivity: the state of being passive.

pH: The negative logarithm of the hydrogen ion activity written as: $pH = -\log(a_H^+)$, where $a_H^+$ = hydrogen ion activity or molar concentration of hydrogen ion multiplied by the mean ion-activity coefficient.

Pitting: Localized corrosion of a metal surface that is confined to a small area and takes the form of cavities called pits.

Pitting factor: The ratio of the pit depth of the deepest pit resulting from corrosion divided by the average penetration as calculated from mass loss.

Plankton (planktonic): Microorganisms floating or drifting in a body of water.

Plastic deformation: Permanent deformation caused by stressing beyond the elastic limit.

Plasticity: The ability of a metal to deform permanently (nonelastically) without fracturing.

Polarization: the change from the open-circuit potential as a result of current across the metal/electrolyte (water) interface.

Postweld heat treatment: Heating and cooling a weldment in such a way as to obtain desired properties.

Precipitating hardening: Hardening of a metal caused by the precipitation of a constituent from a supersaturated solid solution.

Ryznar index: A calculated saturation index for calcium carbonate that is useful in predicting scaling behavior of waters.

Reduction: Gain of electrons by a constituent of a chemical reaction

Relative humidity: The ratio, expressed as a percentage, of the amount of water vapor present in a given volume of air at a given temperature to the amount required to saturate the air at that temperature.

Rust: Corrosion products consisting of various iron oxides and hydrated iron oxides.

Scaling: The deposition of water-insoluble constituents on a metal surface.

Sensitizing heat treatment: A heat treatment, whether accidental, intentional, or incidental (as during welding), that causes precipitation of constituents (usually carbides) at grain boundaries, often causing the alloy to become susceptible to intergranular corrosion or intergranular stress corrosion cracking.

Sessile: Attached to a surface.

Slime: An extracellular material produced by some microorganisms, characterized by a slimly consistency of various chemical composition.

Spalling: The spontaneous chipping fragmentation, or separation of a surface or surface coating.

Sulfate reducing bacteria (SRB): Any organism that metabolically reduces sulfate to $H_2S$, includes a variety of microorganism (see *Desulfovibrio*)

Sulfide stress cracking: Cracking of a metal under the combined action of tensile stress and corrosion in the presence of water and hydrogen sulfide (a form of hydrogen stress cracking).

Thermal galvanic corrosion: corrosion resulting from a corrosion cell caused by a ther~~mal~~ gradient.

Tuberculation: The formation of localized iron oxide corrosion products in the form of knoblike mounds.

Wrought: Metal in the solid condition that is formed to a desired shape by working (rolling, extruding, forging, etc.) usually at an elevated temperature.

Yeast: A fungus of the family *Saccharomycetaceae* used especially in the making of alcoholic liquors and in leavening bread.

## 13.0 References

### Books and Training Programs

AWT – "The Mentor, Cooling Water Training Program". Association of Water Technologies, Inc. 8201 Greensboro Drive, Suite 300, McLean, VA 22102

Drew – "Principles of Industrial Water Treatment." Drew Industrial Division, Ashland Chemical Company, One Drew Plaza, Boonton, NJ 07005

GEBetz – "Handbook of Industrial Water Conditioning." GEBetz Handbook, P.O. Box 4632, Trenton, NJ 08650-9877
(Can also be obtained from Association of Water Technologies, Inc.)

Nalco – "The Nalco Water Treatment Book." McGraw-Hill Book Co., New York, NY
(Can also be obtained from Association of Water Technologies, Inc.)

Nalco – "The Nalco Guide to Cooling Water system Failure Analysis." McGraw-Hill Book Co., New York, NY
(Can also be obtained from Association of Water Technologies, Inc.)

Frayen – "Cooling Water Treatment Principles and Practice." Chemical Publishing Co., Inc., New York, NY
(Can also be obtained from Association of Water Technologies, Inc.)

Dillon – "Corrosion Control in the Chemical Processing Industries." NACE International, P.O. Box 218340, Houston, TX 77218

Brandvold – "Water Treatment: Industrial, Commercial & Municipal,," Association of Water Technologies, Inc., 8201 Greensboro Drive, Suite 300, McLean, VA 22102

Butler and Ison – "Corrosion and Its Prevention in Water" Reinhold Publishing Corporation, New York, NY

Tanis – "Procedures of Industrial Water Treatment," Ltan Inc., Ridgefield CT
(Can also be obtained from Association of Water Technologies, Inc.)

NACE International – "Basic Corrosion Course." NACE International, P.O. Box 218340, Houston, TX 77218

Cowan & Weintritt – "Water-Formed Scale Deposits." Gulf Publishing Company, Houston, TX

Degrémont – "Water Treatment Handbook." Lavoisier Publishing, 11, rue Lavoisier F-75384 Paris Cedex 08

McCoy – "The Chemical Treatment of Cooling Water." Association of Water Technologies, Inc., 8201 Greensboro Drive, Suite 300, McLean, VA 22102

Fontana – "Corrosion Engineering." McGraw-Hill Book Company, New York, NY.

Mansfield – "Corrosion Mechanisms." Marcel Dekker, Inc. New York, NY

Alcamo – "Fundamentals of Microbiology," Jones & Bartlett, Sudbury, MA

Videla – "Manual of Biocorrosion," Lewis Publishers, Boca Raton, FL.

Geesey et al – "Biofouling and Biocorrosion in Industrial Water Systems," Lewis Publishers, Boca Raton, FL

## Journal Publications

*The Analyst.* Association of Water Technologies, Inc., 8201 Greensboro Drive, Suite 300, McLean, VA 22102

*Material Performance.* NACE International, P.O. Box 218340, Houston, TX 77218

*CTI Journal.* Cooling Tower Institute, P.O. Box 73383, Houston, TX 77273

*Ultrapure Water,* Tall Oaks Publishing, Inc. P.O. Box 621669, Littleton, CO 80162

*Proceedings of the International Water Conference,"* Engineers Society of Western Pennsylvania, Pittsburgh, PA.

# CHAPTER 4
# TRAINING QUESTIONS

1. Why are once-through cooling water systems less susceptible to the formation of mineral scales on heat transfer surfaces compared to open recirculating cooling water systems? Sections 1.0 and 2.0.
2. A closed cooling loop circulates chilled water from a central plant to several campus buildings. After several years of "no problem" operation, the system begins to lose water. It is determined that some of the underground expansion joints have failed due to mechanical stress. Because repairs would be costly and disruptive, management elects to continue operation, adding water and chemicals as needed to maintain proper levels. However, about a year later, severe pitting corrosion failures are discovered in small diameter lateral chilled water lines in the buildings. What happened? How can the problem be corrected? Could the problem have been avoided? Section 2.3.3.
3. A new commercial office building employs ambient (free) cooling as part of its HVAC system operation, to conserve electric power. The system involves complete mixing of chilled water and open condenser water while the system is in free cooling mode. During the summer months, the building operates in free cooling mode from 6:00 AM to 10:00 AM each morning, in normal HVAC mode from 10:00 AM to about 3:00 PM, and in free cooling mode from 3:00 PM to 8:00 PM. The building shuts down at night and on weekends. After about two years in this operating mode, the chilled water system became so severely corroded that leaks were difficult to contain and the building could not maintain effective cooling in hot weather. What went wrong? How should the system have been operated to minimize this problem? What design changes could have been made to avoid the problem? Section 2.4.
4. What is meant by an evaporative condenser, and how does it differ from a normal cooling tower and heat exchanger system? Section 3.2.4.
5. What is film fill in a cooling tower? How does it differ from splash fill and what problems should you be prepared to handle in film fill cooling towers? Section 3.3.
6. Define the terms "approach temperature" and "range" as they relate to cooling towers. Explain how knowledge of the thermal performance of a cooling tower can help in detecting cooling system problems. See section 3.5.1.
7. Define the tonnage rating of a cooling tower. What will be the nominal circulation rate of water in a 1000 ton cooling tower? Section 3.5.2.
8. Define "cycles of concentration". Section 3.5.2 and chapter 1.
9. Define "holding time index", or "half-life" in a cooling tower. Why is this concept important in cooling water operations? Section 3.5.3.

10. A 1000 ton HVAC cooling tower operates at 5 cycles of concentration. The system volume is 27,000 gallons and the temperature range is 15 °F. Calculate the following parameters for this system: Sections 3.5.2 and 3.5.3.
    a. Recirculation rate (R)
    b. Evaporation rate (E)
    c. Blowdown rate (B)
    d. Makeup rate (M)
    e. Holding time index (HTI)

11. What is a "fouling allowance"? In this context, explain why HVAC systems are different from process cooling systems? Section 4.1.

12. A process heat exchanger was originally designed with carbon steel tubes and tube sheets. The tubes corroded, and the plant replaced them with Admiralty brass tubes. What new problem did this change create, and what techniques are available to solve this problem? Section 5.3.

13. What is microbiologically-influenced corrosion (MIC)? What tests should be used to confirm the presence of MIC in a cooling water system? Sections 5.5.3 and 5.5.4.

14. How do corrosion inhibitors work? What are anodic, cathodic and general inhibitors? List some examples of each. What are so-called "dangerous" inhibitors? Section 5.10 and chapter 1.

15. Can austenitic stainless steels, e.g. types 304 and 316, be used in cooling water applications where significant concentrations of chloride ions are present in the water? Explain your answer. How can stainless steels be protected under these conditions? Section 6.5.4.

16. What is white rust on galvanized steel, and how can it be prevented? Sections 6.6.3 to 6.6.5.

17. Explain the three mechanisms by which inhibitors can help prevent mineral scale formation. Section 7.3.

18. Calculate the Langelier Stability Index (LSI) for each of the following waters. Which is more likely to precipitate calcium carbonate scale? Explain your answer. Section 7.4.1 and chapter 1.

| Water | Temp. | TDS | Calcium | M alk | P alk | pH |
|---|---|---|---|---|---|---|
| A | 100 | 300 | 20 | 150 | 65 | 9.0 |
| B | 100 | 300 | 200 | 150 | 0 | 8.0 |

19. What can be learned from LSI calculations about the corrosivity of a water supply or a circulating cooling water? Section 7.4.1 and chapter 1.

20. The first rule for success in any cooling water treatment program should be to keep the system clean. Explain why this is true, and list some of the problems that can result if deposits are allowed to accumulate in a cooling system. Section 8.2 and Chapter 1.

21. Explain the concept of "biocide demand" in an open recirculating cooling water system. Section 9.5.3.
22. What are the differences between oxidizing and nonoxidizing microbiocides? How should each type of biocide be used in open cooling systems? Section 9.5.2.
23. Explain why bromine derivatives are preferred over hypochlorite (bleach) solutions in alkaline cooling systems. Are there any circumstances in which bleach should be used rather than a bromine compound? Sections 9.6 and 9.7, and Figure 4-30.
24. Explain the fundamental differences between closed cooling systems and open recirculating systems. How do these differences affect chemical treatment programs for closed systems? Section 10.4.
25. Explain how a corrosion coupon rack should be designed and how coupons should be installed and evaluated. Section 11.2 and Figure 4-32.
26. How does a linear polarization resistance (LPR) probe work? What are the differences between corrosion rates calculated from LPR data and from corrosion coupons? Section 11.3.
27. Explain the difference between planktonic and sessile bacteria in a cooling water system. How should bacteria counts be taken to obtain as realistic a picture as possible of biofouling conditions in the system? Section 11.5.

## ANSWERS TO CHAPTER 4 TRAINING QUESTIONS

### Answer to Question 1

There are several reasons for this. The most important reason for this is that once-through water does not concentrate, or cycle up as does cooling tower water, so that LSI values are lower. An exception to this is that if the water source is a lagoon or spray pond, evaporation may cause the lagoon water to be two or even three times as concentrated as the original source water.

Also, because the water contacts the heat exchangers only once and for a very short time, the temperature rise is usually negligible. In essence, there is minimal change in the chemical and physical properties of the water.

### Answer to Question 2

Increasing amounts of makeup water brought dissolved oxygen into the system. Closed cooling water treatment programs are designed to operate with little or no dissolved oxygen. The pitting failures were the result of oxygen concentration cell corrosion. Further corrosion can be prevented by adding an appropriate oxygen scavenger to the treatment regime, but this will be a very expensive program in view of the water losses. Management should have been encouraged to “bite the bullet” and repair the faulty expansion joints.

### Answer to Question 3

Short term swings between free and mechanical cooling, with no effort to maintain proper chemical treatment in the chilled water loop, combined with long stagnant periods, led to severe corrosion and fouling damage. The system should not have been operated in free cooling mode unless free cooling could be maintained for days at a time. Whenever the system was switched back from free to mechanical cooling, high dosages of closed system treatment chemicals should have been added to the chilled water system. The system should have been designed with a plate-and-frame heat exchanger separating the condenser water and chilled water systems. This would have permitted trouble-free operation under all conditions, albeit with some loss in cooling efficiency.

### Answer to Question 4

In an evaporative condenser, the cooling coils are directly inside the cooling tower instead of in a separate shell-and-tube heat exchanger. Cooling tower water circulates from the tower basin back to the top of the tower and sprays over the tubes. The tubes are normally galvanized steel. The most common operating problem in these systems is mineral scale deposition caused by evaporation of water on the tubes.

Answer to Question 5

Film fill is a modern design consisting of interlocking corrugated plastic sheets (usually PVC), over which the water flows inside the cooling tower. This creates substantially more surface area than the older splash fill, and therefore more efficient evaporation and cooling.

There are two potential problems that must be considered in film fill cooling towers:

- Because the spacing between the PVC sheets is small, for high efficiency, this space is easily bridged by fouling deposits. These deposits can interfere with water flow, thus reducing cooling efficiency. If the deposits block the fill completely, it may be difficult or impossible to clean the fill. It is therefore very important, in any film fill cooling tower, to prevent mineral scale formation or accumulation of corrosion products, microbiological slimes and other deposits in the fill.
- The PVC sheets are very thin, to minimize the weight of the fill. The fill section lacks strength and structural integrity. Therefore the fill can easily be damaged by rough handling, loose tools, etc. Damaged fill may not fit properly in the tower and may lead to channeling of water and loss of cooling efficiency. Severe fouling can result in the fill collapsing.

Answer to Question 6

- The approach temperature is the difference between the temperature of the cooling water leaving the tower and the wet bulb temperature. Low approach temperatures indicate more efficient cooling, but require larger cooling towers. Design is thus a trade-off between cost and cooling efficiency. Typical approach temperatures fall between about 5 and 20 °F.
- The range is the difference in temperature between the water entering and leaving the tower. The range determines the amount of water that the tower can evaporate. A typical rule of thumb for evaporation is one percent of the circulating water flow for every 10 °F temperature drop across the tower.
- Although other factors can also influence tower efficiency, approach temperatures more than a few degrees above design, and lower-than-design range temperatures, are clear warning signs of possible fouling in the tower. These problems can include blocking of downcomer ports on open deck towers, blocking of air flow through the tower, and fouling of the fill. Action should be taken to correct these problems before serious damage occurs.

Answer to Question 7

The tonnage rating is a measure of the heat transfer capacity of the cooling tower. A 1 ton tower can theoretically transfer 12,000 BTU/hour of heat to the atmosphere. As a rule of thumb, cooling towers circulate approximately 3 GPM of water per ton of capacity. Thus, a 1000 ton tower will circulate about 3000 GPM.

### Answer to Question 8

Cycles of concentration, or "cycles" is a measure of the amount of water evaporated in a cooling tower. Cycles is calculated as the ratio of the concentration of specific ions in the circulating cooling tower water to the concentration of the same ions in the makeup water. Cycles can also be calculated as the ratio of makeup water flow divided by blowdown flow.

### Answer to Question 9

The holding time index (HTI) is the time required for a slug dose of chemical added to the cooling tower basin to dilute down to half of its original concentration. The HTI must be known when calculating dosages of chemicals that are to be slug-dosed to the cooling tower, such as nonoxidizing biocides.

### Answer to Question 10

Use the formulas in sections 3.5.2 and 3.5.3 to calculate these parameters.

a. R = Approximately 3000 GPM
b. E = 36 GPM
c. B = 9 GPM
d. M = 45 GPM
e. HTI = 35 hours

### Answer to Question 11

HVAC systems are expected to operate with clean makeup water and no process or water-side fouling. Therefore, these system are not designed with any excess capacity, or fouling allowance. This allows the cooling systems to operate at acceptable flow rates, but requires well-planned water treatment programs to keep the systems free of corrosion and fouling deposits.

Process heat exchangers, on the other hand, are often designed with a fouling allowance – that is, excess capacity intended to permit the system to accept some fouling and still meet design production rates. However, when these systems are new (clean), the excess capacity forces operators to throttle the cooling water flow to avoid overcooling the process fluid. The resulting low cooling water flow encourages both fouling and corrosion in the heat exchanger and makes water treatment more difficult.

### Answer to Question 12

The brass tubes created a galvanic cell with the steel tube sheet, that could corrode the tube sheet. Techniques to help prevent this corrosion include:

- Use a high level (2-4 mg/L) of active copper corrosion inhibitor to film the brass tubes and any copper that does plate out on the tube sheet.
- Use replaceable zinc or magnesium anodes in the water box to cathodically protect the tube sheet.
- Paint the tube sheet and water box with a protective coating. Coatings are effective, but they must be carefully applied and maintained.

Answer to Question 13

MIC is a form of under-deposit corrosion. It has been identified on most common metals used in cooling water systems, but it is most often found on carbon steel and austenitic stainless steels. MIC is caused by organic acids formed by anaerobic bacteria that collect beneath deposits on metal surfaces. Sulfate-reducing bacteria (SRB) are the most common bacterial species that can cause MIC.

No tests for MIC are specific. Other corrosion processes can produce the same effects. Therefore no single test is sufficient to confirm the presence of MIC. Morphology of corrosion damage, bacterial tests and chemical tests should all be used. At least two, and preferably all three of these tests should be positive to confirm MIC, as described in section 5.5.4.

Answer to Question 14

Corrosion inhibitors interfere with one or more steps in the overall corrosion reaction on steel. Anodic inhibitors form protective films at anodic sites where corrosion occurs, and help prevent the dissolution of iron to form ferrous ions. Chromate (no longer used), nitrite, orthophosphate and molybdate are typical anodic corrosion inhibitors.

Cathodic inhibitors form films that help prevent diffusion of dissolved oxygen to the metal surface, thus interfering with the cathodic corrosion reaction. Zinc and polyphosphates are typical cathodic corrosion inhibitors.

General inhibitors form films that cover the entire metal surface, effectively "insulating" it from the water. Tolyltriazole and filming amines (in boiler systems) are examples of widely-used general corrosion inhibitors.

Anodic inhibitors are sometimes called "dangerous" because they must be applied at sufficient dosage to protect all anodic sites in the system. If not, the entire corrosion current may be concentrated on a few exposed anodic sites. This can lead to serious pitting corrosion. This problem can be made much less serious by using mixed inhibitor formulations that interfere with both the anodic and cathodic corrosion reactions.

Answer to Question 15

Yes, stainless steels can be used in cooling water applications with chlorides present. The problem of chloride-induced stress corrosion cracking (SCC) of stainless steels is often misunderstood and exaggerated. Stainless steels are frequently used for cooling tower basins, for condenser tubes in the utility industry and for process heat exchangers.

SCC on stainless steels is rare below 200 °F, and has never been reported below 160 °F. SCC is also rare in systems with chloride levels below about 200 mg/L. From the water treatment side, the most important things that can be done to protect stainless steels from SCC are to keep the metal surfaces clean and deposit-free, and to avoid stagnant and low-flow conditions. These steps help to avoid anaerobic conditions beneath deposits, where corrosion can occur and chloride ions can concentrate.

Answer to Question 16

*White rust is a nonprotective zinc hydroxycarbonate deposit that forms on new galvanized steel exposed to soft, alkaline water before the normal protective films have had time to develop. White rust can be prevented by starting up new galvanized steel cooling towers with a neutral pH phosphate-based treatment program. Refer also to the separate AWT publication on white rust problems.*

Answer to Question 17

The three mechanisms are:

- Threshold inhibition, or the "threshold effect": Very small, substoichiometric dosages of selected polymers and natural products can interfere with the growth of small crystallites of calcium carbonate, calcium phosphate and other minerals. Since crystal growth is a dynamic process that proceeds simultaneously in both directions, crystallites that cannot grow properly tend to redissolve. This releases the inhibitor for further reactions with other crystallites.
- Crystal distortion: Some distorted crystallites do succeed in growing. However, they exist in unstable crystal "habits" and do not stick to surfaces with other normal crystals. These unstable crystals eventually redissolve.
- Dispersion: If a solution of a mineral scale-forming compound is supersaturated, it will eventually precipitate. Dispersants coat the precipitating crystals as they form and prevent them from sticking to metal surfaces. These crystals may collect as loose sludge in basins and low points in the system. Some will be removed with blowdown.

Answer to Question 18

Both waters have the same LSI value, +0.9. However, water A is much more likely to precipitate calcium carbonate. P alkalinity is not included in the LSI calculation. From Figures 1-9 and 1-10, and Table 1-10 in Chapter 1, it can be seen that most of the alkalinity in water A is carbonate, while in water B the alkalinity is bicarbonate. Calcium carbonate will precipitate quickly in water A. In water B, calcium carbonate will form only as reactions occur that convert bicarbonate ions to carbonate.

If the system is corroding, the higher localized pH on cathodic surfaces (chapter 1) will cause this conversion. This is why calcium carbonate scale forms more rapidly in corroding systems than in non-scaling systems. Also, gradual stripping of carbon dioxide from the tower will raise the pH and convert bicarbonate to carbonate.

The LSI is a general guide to calcium carbonate scaling tendencies, but it should be considered in context with the P alkalinity, the calcium hardness, and the source of the water. Water A is lime-softened, while water B is a natural well water. The fact is, that even though water A is more supersaturated and more likely to precipitate, water B will eventually form more calcium carbonate scale because of the higher calcium content.

Answer to Question 19

Nothing. The terms "scaling" and "corrosive" as commonly used in LSI calculations, do not apply in cooling water systems. The correct terms should be "scaling" and "nonscaling". Waters with both positive and negative LSI values can be very corrosive. Alkalinity, calcium hardness and pH all have important effects on the corrosivity of cooling water, but these effects are not shown by the LSI calculation.

Answer to Question 20

The purpose of any cooling system is to remove heat from, or add heat to, a process or an occupied space. Anything that interferes with heat transfer, or that impacts the integrity of the heat transfer system, makes the system less efficient or inoperable, and increases costs. Problems created by deposits in cooling systems include loss of flow and/or cooling capacity, and system corrosion. Also, it is much easier and less costly to keep a system clean than it is to remove accumulated deposits.

Answer to Question 21

Biocide demand is the amount of any microbiocide that must be added to a cooling system before any free biocide becomes available to react with bacteria and algae. The term applies to both oxidizing and nonoxidizing biocides, although it is most often used with oxidants. It is site-specific for each cooling system.

Oxidizing agents react with organic matter and inorganic compounds such as sulfides and ferrous iron salts. Nonoxidizing microbiocides are often polar organic compounds that adsorb on suspended solids or react with dissolved oxygen and oxidizing agents. These reactions consume biocides so that they are not available; hence the term "demand".

It is very important to know the "demand" for an oxidizing microbiocide in order to determine the dosage required to maintain the desired residual in the water. This can be done by trial and error in the system, or by simple titrations. The demand for nonoxidizing biocides is difficult to determine, and this work is usually not done. These biocides are slug-dosed, and the dosage is adjusted as needed to achieve the expected result.

Answer to Question 22

Oxidizing biocides work by destroying cells. Nonoxidizing biocides are absorbed through cell walls and work by interfering with metabolic processes.

Oxidizing biocides react quickly and have short residual times. They are best applied at continuous low level dosages, although slug dosages are often used to obtain short-term high residual levels. Nonoxidizing biocides as a rule are more expensive than oxidants, but they react more slowly and can exist for much longer times in the system. They are normally applied as intermittent slug doses.

Bacteria are not known to develop resistance to oxidizing biocides. However, bacteria do seem to acclimate to some nonoxidizing biocides, so that larger dosages are required and eventually the biocides become ineffective. To avoid this problem, it is common practice to alternate treatment with two or more nonoxidizing biocides.

The most effective microbiological control programs are often combinations of an oxidizing biocide fed continuously plus intermittent slug doses of two or more nonoxidizing biocides.

Answer to Question 23

Hypochlorous and hypobromous acids are much more effective biocides than the corresponding ionized salts (chapter 1). Because hypobromous acid is a weaker acid, it exists in the acid form at higher pH levels than does hypochlorous acid. Therefore, bromine compounds are generally preferred above pH 8. However, bleach solutions are still effective, at higher dosages. When very high residuals are needed, for example during an alkaline on-line chemical cleaning process, it is usually more cost-effective to use bleach rather than a bromine compound, even though much larger quantities will be needed.

Answer to Question 24

Closed system water circulates in a loop, with no evaporation and negligible blowdown. Thus the water does not concentrate, and it stays in the system for a long time. Chemical treatments must be stable and effective without regular replacement. Since there is effectively no blowdown, there is no easy way to remove suspended solids from the system. Sidestream bag or sand filters should be installed in any closed loop system that contains suspended solids.

Closed systems theoretically contain no dissolved oxygen, and chemical treatment programs are designed to work under these conditions. However, any required makeup water due to leaks, repairs, etc. brings in oxygen. Air can be aspirated in through leaking pump seals, etc. Small amounts of dissolved oxygen can cause serious localized corrosion problems, just as in a boiler. Makeup water, however slight, can also bring in microbiological problems.

For these reasons, chemical treatment of closed systems must never be assumed to be routine. Each system must be surveyed, problems identified, and corrected mechanically if possible. Then an appropriate chemical program can be selected.

Answer to Question 25

The rack must have sufficient pressure drop to provide a minimum flow through the rack of 3 feet per second, equivalent to 8 GPM through 1 inch pipe or 5 GPM through ¾ inch pipe. Water flow must be from the bottom to the top of the rack, and the rack must include a flowmeter for monitoring and adjusting flow.

The rack can be made from PVC pipe for easy construction. However, steel pipe provides a unique opportunity to inspect the internal surfaces over time. The rack should include a spool piece that can be removed for destructive inspection on a regular basis.

Coupons must be installed horizontally, with the coupon surfaces in a vertical plane. Steel coupons should be at the bottom of the rack and copper at the top. Water flow must be from the coupon holder out over the coupon, never the reverse.

Coupons should be removed for inspection at approximately 90 day intervals. Shorter times produce exaggerated corrosion rates. Coupons should be photographed as removed, to provide an ongoing record of system conditions.

Answer to Question 26

LPR probes work by setting up a small potential difference between two identical electrodes exposed in the system, and measuring the resulting current flow. This current is influenced by the nature of the metal surfaces and by any corrosion in progress. From these data, the LPR instrument calculates a corrosion rate. This calculated rate is a function of corrosion rates in the system, but it is not an exact measure and may, in fact, differ appreciably.

LPR data are "instantaneous" corrosion rates, calculated at the time the measurements were made. Coupon data, on the other hand, are average corrosion rates over the period of exposure.

LPR data can be plotted as a trend graph, and can produce useful real time information, e.g. loss of inhibitor feed, slug addition of an oxidizing biocide, etc.

Answer to Question 27

Planktonic bacteria are free-floating in the circulating water. They are easily sampled by dipstick methods, for example. Planktonic counts provide specific information about the microbiological population in the water, but only general indications of possible biofouling of metal surfaces in the system. Also, since open recirculating cooling water is well aerated in the cooling tower, planktonic counts are not a reliable indicator of possible anaerobic populations in system deposits. Low planktonic counts are reassuring, but in fact tell very little about possible microbiological deposits in the system. High planktonic counts, on the other hand, are an indication that there is a reservoir of microbiological fouling in the system, probably on pipe walls or in low flow areas.

Sessile bacteria counts must be taken by sampling deposits: on basin walls, in coupon racks, pump strainers, etc., and in system piping when possible. Low sessile counts are good news; high sessile counts are a sure sign of biofouling.

Biofilm pressure drop monitors and coupons made from folded stainless steel wire mesh screening are two useful methods for monitoring sessile biofilm formation.

# CHAPTER 5

## Regulatory Compliance for the Water Treatment Industry

## Table of Contents

# CHAPTER 5

# Regulatory Compliance for the Water Treatment Industry

## 1.0 Introduction

Regulations governing the handling and use of hazardous chemicals are an ever-growing concern in industry in general, and in the water treatment industry in particular. Since the early 1970's the number of regulations affecting hazardous chemicals has increased dramatically and the emphasis on compliance and enforcement continues to rise as new regulations are added and as technology improves. These regulations are designed to protect the environment from chemical contact, workers from exposure to chemicals while performing their duties, and the general population from releases of hazardous chemicals in commercial transportation and from releases from neighboring industrial facilities.

Everyone in the chemical handling "chain" – that is, anyone involved in chemical manufacturing, packaging, selling, distribution, end-use, and disposal – is affected to some extent by these regulations. Non-compliance is serious business for those who are harmed by chemical exposure and for those who must pay the penalty (both financial and criminal) for that exposure. Ignorance of the regulations is no excuse and in today's business climate when awareness of regulations is at an all time high a plea of ignorance is an indication to government agencies of business irresponsibility and negligence.

This chapter is intended to give the water treatment professional an orientation to regulations that particularly affect the water treatment industry. It is not all-inclusive, and regulations are changing all of the time. Nevertheless, the basic information in this chapter helps to lay a solid foundation toward compliance and safe handling of hazardous chemicals. References for more information are also provided.

This chapter covers regulations promulgated at the federal level by the three primary agencies with authority to regulate hazardous materials. These are:

- The Environmental Protection Agency (EPA).
- The Occupational Safety and Health Administration (OSHA).
- The Department of Transportation (DOT).

Important bodies of regulations are reviewed here, many of which are broken down into several components. Some regulations are basic in their application, while others are very extensive. This chapter also addresses how the regulations particularly apply to the water treatment industry and it discusses the role of good product stewardship.

Many states and municipalities also have agencies that address hazardous chemical use. State and local regulations will often be more stringent than federal regulations, which set the minimum standards. Industry may be directly regulated by a federal agency as well as by state and local agencies.

## 2.0 The Environmental Protection Agency (EPA)

Among many other responsibilities, the Environmental Protection Agency (EPA) is charged by Congress with regulating the emission and discharge of hazardous materials into the environment. This includes deliberate or accidental emissions or discharges into the atmosphere, soil, or water supplies (both ground and surface waters). Handling of hazardous wastes and emergency response planning and actions are also within the EPA' s domain of regulations.

Water treatment professionals, as well as their customers who use hazardous materials, are subject to many of the EPA s regulations. EPA regulations can be found in the Code of Federal Regulations 40 series (40 CFR). See also the EPA website at www.epa.gov. Important pieces of EPA regulations include:

- The Clean Air Act.
- The Clean Water Act.
- The Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA).
- The Superfund Amendments and Reauthorization Act (SARA).
- The Resource Conservation & Recovery Act (RCRA).

These are the regulations that are discussed in this chapter.

### 2.1 THE CLEAN AIR ACT

The Clean Air Act was originally passed by Congress in 1963 to regulate hazardous air pollutants and has been amended 16 times, with the most recent amendments in 1990. The 1990 amendments resulted in the regulation of sources of air pollution in addition to the individual pollutants. The Clean Air Act consists of six titles of regulations:

I. Air Pollution Prevention and Control (Ozone, Carbon Monoxide, Particulates, Sulfur Oxides, Nitrogen Dioxide, Lead)
II. Emission Standards for Moving Sources
III. General
IV. Acid Deposition Control
V. Permits
VI. Stratospheric Ozone Protection

Water treatment companies and their customers are potentially subject to Title III of the Clean Air Act. This part of the act covers hazardous air pollutants, volatile organic compounds (VOC), and other regulated substances that may be released to the atmosphere. Hazardous air pollutants (HAP) in particular must be reported if 10 tons of any single HAP or 25 tons of any combination of

HAPs are released annually. An amendment to this section establishes the Risk Management Program (RMP) for facilities that maintain regulated substances above established threshold quantities (TQ). *Facilities covered by this act may be required to file a permit for each emitting source under Title V.*

A list of the 189 hazardous air pollutants subject to reporting can be found in section 112(b) of the Clean Air Act and lists for 77 toxic and 63 flammable chemicals subject to the RMP can be found in 40 CFR Part 68.130. Chemicals of concern in the water treatment industry include, but are not limited to, ammonia, bromine, chlorine, cyclohexylamine, fuel-based products, hydrazine, hydrochloric acid, and hydroquinone. In most cases, water treatment companies are not heavily regulated by the Clean Air Act. However water treatment customers may be heavily regulated, so it is important to determine how water treatment product use may affect the customer's status and compliance with the Clean Air Act.

The EPA offers a "Plain English Guide to the Clean Air Act" at:
www.epa.gov/oar/oaqps/reg_caa/pegcaain.html .

## 2.2 THE CLEAN WATER ACT

The Federal Water Pollution Control Act was enacted in 1956 to protect the waters of the United States from increasing pollution and to maintain the integrity of the water supply then was completely replaced in 1972. It has been amended several times. The Clean Water Act is a very important regulation for water treatment companies. Water treatment companies and their customers may be subject to these regulations in a variety of ways. EPA offers a "Water Topics Page" which is a thorough source for more information on the Clean Water Act. This page can be found at: www.epa.gov/ebtpages/water.html .

### 2.2.1 Toxic and Pre-treatment Effluent Standards

Industrial uses of chemicals that result in discharges of wastewater (such as boiler blowdown, cooling tower bleed, or tank rinsates) to the local municipal publicly owned wastewater treatment plant (POTW) may require a local permit. These permits will detail any priority pollutants and their effluent limits, as well as other effluent standards such as pH, BOD content, total suspended solids allowable (commonly referred to as sludge), etc.

Molybdenum also falls under regulations found in 40 CFR 503 which restricts the constituents in sludge that can be applied to land. POTW's are stringently regulated on their sludge generation, resulting in their strict permitting and monitoring of product discharge that effects sludge. At the federal level, molybdenum has a ceiling level of 75 mg/kg sludge. POTW's may establish stricter levels. Monitoring of the discharge may be required. Discharge to POTW is critical as the POTW must treat the water so that it may then be provided once again to consumers.

### 2.2.2 Point Source Discharges to Waters of the United States

Companies that have any point source (pipes, ditch, channel, container) discharges to any bodies of water, including surface waters or ground waters, are required to be permitted under the National Pollutant Discharge Elimination System (NPDES), except as it effects permitting by the local POTW. NPDES permits are typically issued by the state and therefore can vary widely in their standards. States may regulate bodies of water in a variety of ways. NPDES permits may be substantially different from one another (for example, Chesapeake Bay may be more stringently regulated than a lake in another state). Therefore, it is almost impossible to definitively describe criteria for NPDES permits in a broad sense. Monitoring of the discharge may be required.

### 2.2.3 Stormwater Runoff

Any industrial activities, including manufacturing or storage, on property where materials are exposed to stormwater, require permitting. Companies that conduct such activities but prevent stormwater contamination may apply for a "No Exposure Certification" for exclusion from NPDES Storm Water Permitting. Stormwater permits are also issued at the state level. Companies that combine storm and sanitary systems may be exempt from these regulations but many states will require a "No Exposure Certificate" in these instances as well. Generally, stormwater must be contained and evaluated prior to release to drainage ditches. Monitoring of the stormwater discharge prior to release may also be required.

### 2.2.4 Pesticide Formulator, Packager, and Repackager (PFPR) Discharge

A business that has biocides present at its facility may be subject to these regulations if it is engaged in blending, packaging or repackaging biocides. If there is a potential of any discharge of a biocide to the POTW, then the POTW must be notified in writing of that potential and those discharges may be addressed in the permit for the individual facility. Any potential discharge of biocides to surface waters or ground waters must be addressed in the NPDES permit.

Formulators, packagers, and repackagers of biocides fall under a separate body of regulations for biocide discharge. EPA's goal for facilities engaged in these activities is zero-discharge of biocides. These regulations are known as the P2 Alternative for pollution prevention. An excellent source for detailed information on these regulations is the Pollution Prevention Guidance Manual for the Pesticide Formulating, Packaging, and Repackaging Industry. This manual can be accessed at: www.epa.gov/guide/p2/pdf/p2guide.pdf .

Discharge of biocides when used in a treatment process is not covered by the PFPR regulations but are addressed at the state or local level in the POTW or NPDES permit for the particular facility the permit covers.

## 2.3 FEDERAL INSECTICIDE, FUNGICIDE, AND RODENTICIDE ACT (FIFRA)

### 2.3.1 Overview

EPA registers and regulates antimicrobial pesticides under the Federal Insecticide, Fungicide and Rodenticide Act (FIFRA). Congress enacted FIFRA in 1947 in order to regulate the use of pesticides. The law was primarily and still is a labeling law. The United States Department of Agriculture (USDA) was the regulatory agency responsible for FIFRA, but in 1970, President Nixon established the United States Environmental Protection Agency (EPA) and charged this Agency with the responsibility of regulating pesticides. Pesticides include antimicrobial pesticides, or biocides as they are commonly referred to in the water treatment industry.

Antimicrobial pesticides, such as disinfectants & sanitizers, are pesticides that are intended to "(i) disinfect, sanitize, reduce, or mitigate growth or development of microbiological organisms; or (ii) protect inanimate objects (for example floors and walls), industrial processes or systems, surfaces, water, or other chemical substances from contamination, fouling, or deterioration caused by bacteria, viruses, fungi, protozoa, algae, or slime." This category does not include certain pesticides intended for food use; but does encompass pesticides with a wide array of other uses. For example, antimicrobial pesticides act as preserving agents in paints, metalworking fluids, wood supports, and many other products to prevent their deterioration. Individuals applying pesticides must do so in a manner not only consistent with federal laws, but also consistent with state laws and regulations, which differ from state to state.

Companies that develop and manufacture a biocide must register that product. They are considered the primary registrant for that biocide. They may then allow other companies to distribute the biocide under the private label of these companies. Such companies must obtain a supplemental registration. Biocides must be registered at the federal level and approved for use and distribution at the state level. Most states also requires annual reporting of biocide distribution within the respective state as well as the payment of annual maintenance fees.

Any facility that formulates, packages, and repackages biocides must obtain an EPA establishment number. There are also very stringent and detailed requirements for biocide product labels. An additional requirement is the reporting of any *alleged* adverse effect resulting from exposure to a biocide. These reports are submitted through companies that hold primary registrations for the formulating of biocide products.

A key component to these rules is the intended use of a product. A biocide may only be used for and in the manner described on the EPA approved label. **For example a biocide approved for use in swimming pools may be not**

**be used for cooling towers. Also, a biocide may only be applied at a dosage no higher than the maximum specified on the EPA label.**

### 2.3.2 The Primary EPA Biocide Registration Process

Most water treatment companies do not manufacture active biocidal products, and therefore they are not concerned with the EPA primary biocide registration process. They obtain supplemental registrations from the primary manufacturer, as explained above. However, it is important to understand the complexities of the primary registration process because it determines where and how specific biocides can be used by supplemental registrants. The following paragraphs describe the basic process of obtaining a primary registration for a new microbiocide.

To obtain registration, manufacturers of antimicrobial products must meet two basic standards:

1. That the product will not cause unreasonable adverse effects to human health or the environment.
2. That product labeling and composition comply with the requirements of FIFRA.

Moreover, manufacturers are required to submit to EPA detailed and specific information concerning the chemical composition of their product; labeling that reflects the required elements for safe and effective use; effectiveness data to document their claims against specific microorganisms and to support the directions for use provided in labeling; and toxicology data to document any hazards associated with use of the product.

The process of registering a pesticide is a scientific, legal, and administrative procedure through which EPA examines the ingredients of the pesticide; the particular site or crop on which it is to be used; the amount, frequency, and timing of its use; and storage and disposal practices. In evaluating a pesticide registration application, EPA assesses a wide variety of potential human health and environmental effects associated with use of the product. The producer of the pesticide must provide data from tests done according to EPA guidelines. The process may take from months to years to complete, depending upon the complexity of the application and the amount of performance and toxicity data available.

These tests evaluate whether a pesticide has the potential to cause adverse effects on humans, wildlife, fish, and plants, including endangered species and non-target organisms, as well as possible contamination of surface water or ground water from leaching, runoff, and spray drift. Potential human risks range from short-term toxicity to long-term effects such as cancer and reproductive system disorders. EPA also must approve the language that appears on each pesticide label. A pesticide product can only be used legally according to the directions on the labeling accompanying it at the time of sale.

Following label instructions carefully and precisely is necessary to ensure safe use.

### 2.3.3 Types of Registrations

There are several types of registration actions through which pesticides may be used in the United States:

- Federal Registration Actions: Under Section 3 of FIFRA, EPA can register pesticides for use throughout the United States. Some pesticides are registered by EPA for more limited use in certain states. In addition, States, Tribes and Territories can place further restrictions on pesticides, EPA-registered products used or sold within their own jurisdictions.
- Experimental Use Permits (EUPs): Under Section 5 of FIFRA, EPA can allow manufacturers to field test pesticides under development. Manufacturers of conventional pesticides are required to obtain experimental use permits before testing new pesticides or new uses of pesticides if they conduct experimental field tests on 10 acres or more of land or one acre or more of water.
- Emergency Exemptions: Under Section 18 of FIFRA, EPA can allow State and Federal agencies to permit the unregistered use of a pesticide in a specific geographic area for a limited time if emergency pest conditions exist. Usually, this arises when growers and others encounter a pest problem on a site for which there is either no registered pesticide available, or for which there is a registered pesticide that would be effective but is not yet approved for use on that particular site. Also, exemptions can be approved for public health and quarantine reasons.
- State-Specific Registrations: Under Section 24(c) of FIFRA, States can register a new pesticide product for any use, or a federally-registered product for an additional use, as long as there is both a demonstrated "special local need," and a tolerance, exemption from a tolerance, or other clearance under FFDCA. EPA can disapprove a State's special local need registration.

### 2.3.4 Supplemental Registrations

In addition to the above registrations, any registrant having a primary registration under Section 3 of FIFRA can distribute the product through a "supplemental distributor." These registrations are know as a "supplemental distributor registration." The registrant files a "Notice of Supplemental Distribution" with EPA and the completed form must have the concurrence and signature of both the primary registrant and the distributor. All conditions of the primary registration apply equally to the distributor product. It is the responsibility of the primary registrant to see that all distributor labeling is kept in compliance with the requirements placed on the basic product.

As pointed out above, supplemental registrants are required to report any *alleged* adverse effect resulting from exposure to a biocide. These reports are submitted to the primary registration holder, who in turn sends the information to the EPA.

### 2.3.5 Sources for More Information

The following web sites will provide specific/additional information on the FIFRA registration process:

www.epa.gov/pesticides/
www.epa.gov/oppad001/
www.epa.gov/pesticides/registrationkit/
www.epa.gov/opprd001/forms/index.htm/
www.epa.gov/ebtpages/pesticides.html/

The full texf of FIFRA may be accessed at www.epa.gov/pesticides/fifra.htm.

## 2.4 SUPERFUND AMENDMENTS AND REAUTHORIZATION ACT (SARA)

The Superfund Amendments and Reauthorization Act (SARA) was implemented in 1986 following a series of catastrophic chemical releases including the release in Bhopal, India at a Union Carbide plant in 1984. These amendments introduced several new bodies of regulations, including Title III which is also known as the Emergency Planning and Community Right-To-Know Act (EPCRA). EPCRA mandates that the general public has a right-to-know about what hazardous materials are being stored and released into the environment in their communities. These requirements are codified in 40 CFR Parts 355, 370, and 372. An excellent detailed summary of these regulations may be found at: www.epa.gov/region08/toxics/epcra/epcra.html .

In general, this standard applies to any business, regardless of size, that may have present a regulated amount of hazardous chemicals. Regulated amounts of chemicals are specified on appropriate lists for respective reporting requirements. Exemptions do exist for some requirements. Water treatment professionals using ammonia, bromine, cyclohexylamine, hydrazine, hydrochloric acid, hydroquinone, phosphoric acid, potassium hydroxide, sodium bisulfite, sodium hydroxide, sodium hypochlorite, and sodium nitrite may be particularly affected by these regulations. This list is not all-inclusive and some elements of SARA apply to all hazardous materials.

The SARA Title III standards break down into emergency planning and notification, reporting requirements, and general provisions.

### 2.4.1 Emergency Planning and Notification

SARA mandated that each state must establish a State Emergency Response Commission (SERC) that would in turn designate emergency planning districts. Local Emergency Planning Committees (LEPC) were appointed for each district and have the primary responsibility for preparing and implementing emergency response plans for their respective districts. Facilities which handle Extremely Hazardous Substances (EHS) as listed in 40 CFR Part 355, Appendix A are required to notify their SERC, LEPC, and the local fire department that they are subject to SARA Title III reporting requirements. Facilities subject to this section/part of the regulations are also required to designate a facility coordinator to assist the local emergency planning commission (LEPC) in developing emergency plans and are required to inform the LEPC of the identity of the facility coordinator.

### 2.4.2 Emergency Release Reporting

A release of hazardous materials is reportable under SARA Title III if it enters the environment in amounts equal to or in excess of the reportable quantity (RQ) listed for the EHS or hazardous substance. RQs can be found for EHS on the EHS List (Part 355, Appendix A and Appendix B) and they can be found for other hazardous substances on the Comprehensive Environmental Response, Compensation, & Liability Act list (40 CFR Part 302, Table 302.4). This notification must occur immediately once the release has been discovered, and a written follow-up is required as soon as practical. Notification must be made to the SERC, LEPC, and in some cases to the National Response Center.

### 2.4.3 Material Safety Data Sheet Submissions

Any business that is required by OSHA to develop or maintain Material Safety Data Sheets (MSDS) must submit a copy of its MSDSs or a list of chemicals covered by MSDS to the LEPC, the SERC, and the fire department with jurisdiction over the facility. Any listed EHS present at the facility at the time of reporting, or at any one time within the preceding year in amounts of or over 500 pounds (or 55 gallons) or the TPQ, whichever is less, requires MSDS or list submission. Any OSHA hazardous chemical present at the time of reporting or at any one time within the preceding year, in amounts of 10,000 pounds or more, requires MSDS or list submission. These MSDS or the list must be submitted within the first 3 months after a facility becomes subject to this regulation based on meeting or exceeding the threshold quantities described above. Any new chemical that is subject to the regulation that is added, or any significant change to an MSDS of a regulated chemical, triggers the submission of a new list or MSDS within 3 months of the addition or change.

### 2.4.4 Tier Reports

SARA requires facilities to submit a Tier I or Tier II report by March 1 of each year. This report is submitted to the SERC, the LEPC, and to the local Fire Department. Any EHS present in excess of 500 lbs or the listed TPQ on any given day during the calendar year and any other hazardous substance present in excess of 10,000 pounds on any given day during the calendar year must be reported. This hazardous chemical inventory report gives emergency planners the ability to identify high-risk facilities in order to coordinate response activities.

### 2.4.5 Toxic Chemical Release Report/Form R

Facilities must submit an EPA Form R, "Toxic Chemical Release Inventory Reporting Form" by June 30 of each year, covering the period of the previous calendar year, if they meet the following criteria:

1. Facility has 10 or more full-time employees, and
2. Facility operates in Standard Industrial Classification (SIC) major group codes: 10 (except 1011,1081, 1094), 12 (except 1241), or 20 through 30; or SIC codes 4911, 4931, 4939, 4953, 5169, 5171, or 7389, and
3. Manufactured, processed, or otherwise used a listed toxic chemical in excess of threshold amounts.

The chemicals subject to Form R reporting can be found in 40 CFR Part 372.65. The threshold quantity for reporting is based on whether the chemical is manufactured, processed, or otherwise used by the facility. The planning quantities are as follows:

- Manufactured or processed: 25,000 pounds during the calendar year
- Otherwise used: 10,000 pounds during the calendar year

Manufacturers and distributors are required to notify buyers of their products of Form R regulated pollutants that are contained in those products. This requirement can be met by identifying those constituents on the product Material Safety Data Sheet (MSDS). This body of regulation is often referred to as SARA 313 in reference to the section of the Act itself in which these requirements appear.

## 2.5 RESOURCE CONSERVATION & RECOVERY ACT (RCRA)

RCRA is the body of regulations which identifies and governs the disposal of hazardous wastes. These regulations can be found in 40 CFR Parts 260 to 268. RCRA was passed by Congress in 1976 as an amendment to the Solid Waste Disposal Act which focused on traditional forms of trash such as paper, garbage, cans, and glass. Hazardous wastes are identified on a variety of lists based on specific chemicals or their process use. Some hazardous wastes are also based on the hazard characteristic they exhibit such as ignitability, corrosivity, reactivity, and toxicity. The majority of liquid rinsates or other waters generated are not considered hazardous wastes by virtue of the "domestic sewage exclusion" in 40 CFR 264 which generally exempts waters discharged to local POTWs from hazardous waste classification. Other liquids that are able to be recovered and recycled in a manufacturing process or that can be reused without any treatment may also be excluded from classification as a hazardous waste.

EPA regulates hazardous wastes based on the amount of hazardous waste a business will generate during a monthly period of time. There are three categories:

| | |
|---|---|
| Large quantity generator | Generate 300 gallons or 2200 pounds of hazardous waste per month (about five 55 gallon drums). |
| Small quantity generator | Generate 25 to 300 gallons or 220 to 2200 pounds of hazardous waste per month (about one to five 55 gallon drums). |
| Conditionally Exempt | Generate less than 25 gallons or 220 pounds of hazardous waste per month (about less than half of a 55 gallon drum). |

The requirements are more stringent as the generator status increases. Requirements include specific disposal requirements, unique labeling of hazardous wastes, obtaining an EPA hazardous waste facility identification number, storage quantity limitations, storage location requirements, and unique shipping requirements. More information can be found at www.epa.gov/ebtpages/wasthazardouswaste.html.

## 2.6 EPA PENALTIES

EPA penalties may range as high as $70,000.00 per violation per day. Willful intent or failure to take corrective actions may also result in imprisonment. More information can be found at: www.epa.gov/ebtpages/complianceenforcement.html.