Energy conservation measures frequently result in the installation of heat exchangers, cooling jackets, or other devices, to reclaim the heat content of the vent steam containing the noncondensables. Many of these devices cause a backpressure on the vent line and thus restrict flow. The result is higher noncondensable gases in the deaerator effluent.

In some cases, vent steam flow is reduced because of a choked or plugged orifice. Steam may condense in vertical or non-vertical vent pipes. This condensate flows back down the pipe walls, choking the vent orifice when steam flow is not sufficient. To minimize this type of problem, vent piping should be installed with no sharp bends or traps that could pool condensation and obstruct the flow of gases. Cooling water leaks in an external vent condenser, can cause excess water accumulation in the shell. If the drainpipe cannot discharge the excess liquid or is plugged, gas flow to the vent will be restricted.

Proper venting of a deaerator should result in a strong visible plume. There should be an invisible or clear area of approximately 6 to 18 inches (150–460 mm) between the end of the vent pipe and the visible portion of the plume. Irregular spitting of water with the vent discharge can indicate condensation, internal leaks, or water entrainment from broken or damaged spray nozzles. This condition, whatever the cause, can choke the vent gas flow.

Typically, the maximum quantity of steam required for venting a properly operating deaerator is less than 0.2% of the feedwater flow. This value varies relative to the percentage of fresh makeup used, but is less than 0.2% for tray or spray deaerators operating with 100% makeup. Some deaerator manufacturers might conservatively recommend 0.5% to assure sufficient venting.

Mixing Condensate and Makeup

One role of the deaerator is as a receiver for a variety of water, steam, and hot condensate streams that need to be recovered. It is important that these be introduced into the deaerator in such a manner as to avoid extreme temperature interfaces and to permit smooth operation.

A common practice is the separate introduction of the return condensate and cold makeup streams into the deaerator water box or preheater sprays. A large temperature differential between the two streams [more than 80°F (44°C)] can result in thermal stresses and water hammer that can damage deaerator components.

Separate condensate and makeup connections can significantly affect performance in a tray-type deaerator. The amount of mixing that actually occurs in the water box is minimal, and the water spraying out of the water box tends to divide the preheater and tray sections into hot and cold zones. This creates an imbalance of steam flow through the tray stack with the steam gravitating to the cold side. The performance impact of this condition will depend on the temperature difference between zones.

A condensate receiver operating at atmospheric pressure upstream of the deaerator can help provide system stability. Its function is to receive and mix the makeup and condensate such that their flows and temperatures will be smoothed prior to introduction into the deaerator. This alleviates the problem of thermal stresses, water hammer, or performance degradation caused by separate makeup and condensate connections at the deaerator.

The condensate receiver should ideally be located downstream of the heat recovery equipment so that it can vent any free air or noncondensables released by the temperature increase. It should be constructed of stainless steel or lined properly to accommodate the more aggressive water resulting from the mix of cold, oxygen-laden makeup and hot condensate. Water inlets should be designed at opposite sides near the top, and the suction outlet should be at the bottom. The vessel needs to be sized for low-flow velocity and good mixing so that free air release will occur. A check valve should also be included in the line from receiver to deaerator to prevent backflow during shutdown.

If a condensate receiver is absent and cannot be installed, the use of separate condensate and makeup connections should still be avoided. This can be accomplished by joining the two flows at a stainless steel tee connection prior to their entry into the deaerator. The connection should be located a minimum of ten inlet pipe diameters upstream of the deaerator to assure good mixing. A stainless steel tee is required because the blend of cold makeup water and hot steam condensate is extremely corrosive, and mild steel piping will corrode and fail prematurely.

Pressure Deaerator Problems

Poor deaerator performance is usually the result of either a mechanical malfunction or improper operation, especially flow control. Improperly operating deaerators are usually the result of one or more of the following factors:

- Inadequate venting
- Inadequate quantities of steam or steam pressure fluctuation
- Wide fluctuations in feedwater flow
- Feedwater flow rates outside design specifications (above or below)
- Insufficient differential between the influent feedwater temperature and the saturation temperature for the operating steam pressure
- Malfunctioning (plugged or broken) or missing spray nozzles, trays, or atomizing valves

These problems will usually be indicated by a broad temperature differential [>4°F (2.2°C)] between the dome (deaerating section) and the storage section of the unit and by excessive dissolved oxygen in the effluent (more than 15 µg/L for deaerators or more than 60 µg/L for deaerating heaters).

Vacuum Deaerators

Vacuum deaerators remove oxygen and other gases from water at temperatures below the atmospheric boiling point. In some instances, it is undesirable to heat water to accomplish full deaeration, or steam is unavailable to operate pressure deaerators. Examples are process water applications in synthetic fiber plants, desalination, beer and soft drink bottling plants, downhole injection water for water-flood enhanced oil production, water distribution systems, and other processes requiring gas removal without an increase in product temperature. The process is sometimes referred to as cold water deaeration.

The principles employed in vacuum deaeration are the same as those previously described for pressure deaeration, except that the water is not heated to steam temperature. Rather, the water is brought to the boiling point without being heated by lowering its pressure with vacuum equipment. The amount of vacuum necessary is dictated by the vapor pressure of the water at its ambient temperature. For instance, water at 41°F (5°C) will boil in a vacuum of 29.7 inches mercury (754 mm Hg), which corresponds to a pressure of 0.13 psia (0.9 kPaa). At 68°F (20°C), the vacuum required is 29.2 inches mercury (742 mm Hg) or 0.34 psia (2.3 kPaa).

The water vapor produced under vacuum is mixed with oxygen and other noncondensable gases. Low partial pressures of these gases are maintained at the steam/water interface, because of dilution by the water vapor and continuous removal by the vacuum system. Agitation and surface exposure is partially accomplished by spraying the water through spray nozzles or perforated spray pipes. The thin curtains and small droplets of water facilitate diffusion of all gases into the vapor phase in a manner similar to the preheater section in a pressure deaerator. Initial spraying removes the bulk of the noncondensable gases present in the inlet water. Additional agitation is provided by allowing the water to trickle down over trays or suitable random synthetic packing. The vapor, contaminated with the removed gases, is extracted from the unit by the vacuum equipment, condensed where possible, and discharged to waste.

The deaerated water is collected in the integral storage section and pumped to the point of use. Because of the vacuum held in the unit, the deaerator must be elevated at a height suitable for the transfer pump net positive suction head (NPSH) requirement. In addition, the vessel must be designed to withstand full internal vacuum conditions without any penetration of air, that is, it must be perfectly airtight.

The temperature of the water to be deaerated has a marked effect on the physical design of the unit as well as the required capacity of the vacuum equipment. Vacuum is exerted on the vessel using vacuum pumps or, if motive steam is available, multistage steam jet ejectors with inter-condensers. In applications where motive steam for ejectors is unavailable, vacuum pumps must be used, and capital costs can be very high.

Deaerating Condensers

Under favorable conditions and with the proper design, the steam condenser (Fig. 10.13) is probably as good as any available pressure deaerator. Condenser deaeration is performed under vacuum, and many of the principals are the same as previously discussed for vacuum deaeration. A significant difference, however, is that air inleakage is always present in steam condensers.

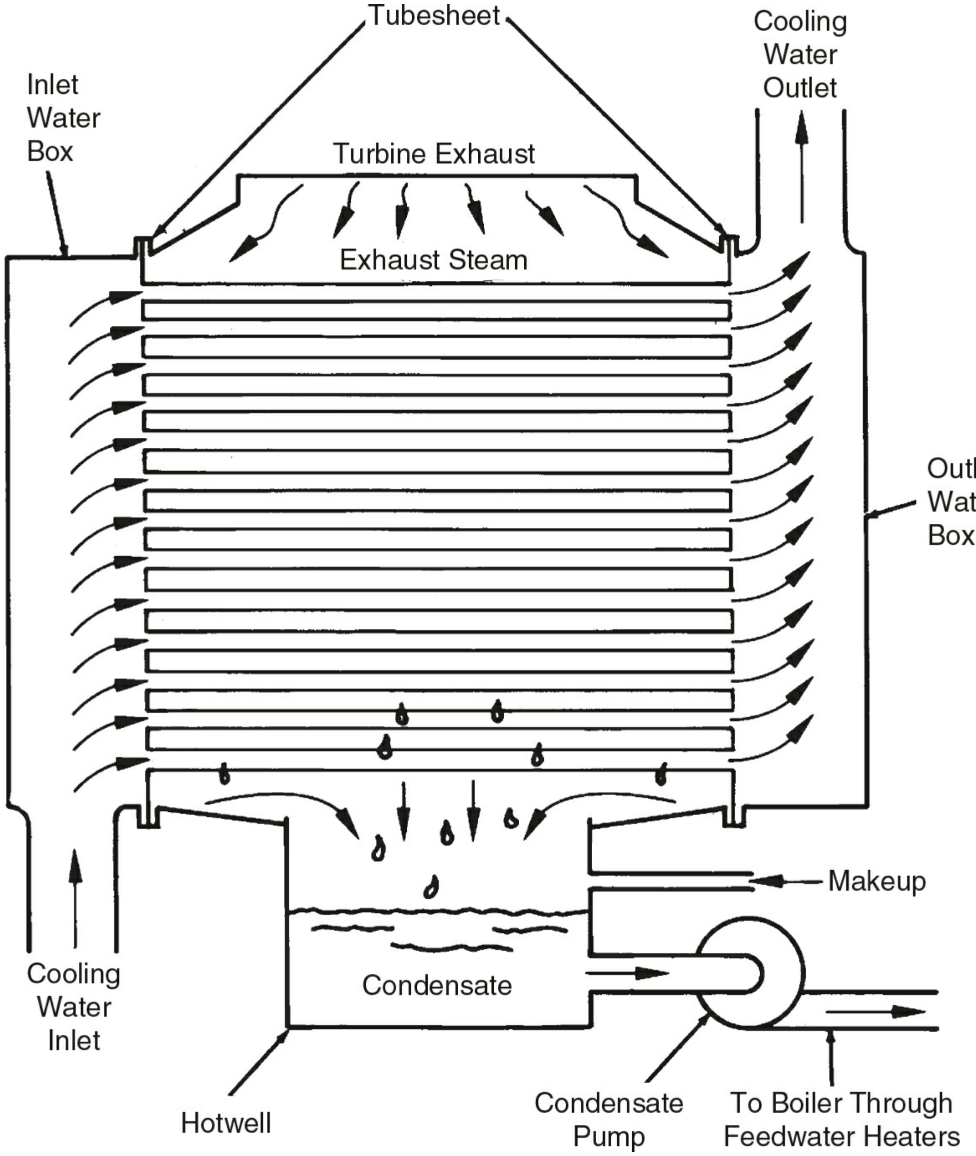


FIGURE 10.13 Basic surface condenser (side view).

Turbine condensers in high-pressure power plants are normally very efficient in reducing noncondensables (including oxygen) in the steam condensate, when operating at full load with less than 3% makeup and low air inleakage. However, during low-load operations:

- Condenser air inleakage rates increase as more equipment operates under vacuum.
- The resultant increased vapor tends to overload the vent system at the same time as the vent system capacity is reduced at lower condenser

pressures.

- Steam distribution deteriorates within the condenser as the reduced heat load allows the majority of the steam to be condensed in the outer peripheral tubes. Noncondensables are neither limited to nor concentrated in the center of the tube bundle, where the vacuum pump suction piping is normally located.
- Condensate subcooling increases as the heat load is reduced.
- Condensers become less effective in deaeration.

At loads other than full load, deaeration efficiency can be improved by installation of a steam bubbler deaerator in the hotwell. This device is similar in some respects to the steam scrubber in a spray deaerator.

In combined cycle heat recovery steam generation (HRSG) plants, where the percentage of makeup water is higher than in conventional power plants, some plants have been retrofitted with vacuum deaerators that treat all makeup water using steam from the condenser. The deaerated makeup is added to the condensate from the condenser tubes and falls into the hotwell.

Feedwater Tanks

Feedwater tanks are typically installed in low-pressure plants [usually less than 100 psig (689 kPag)] that are not equipped with deaerators or some other type of deaerating equipment. Some manufacturers promote them for use with firetube boilers or commercial hot water heaters.

The feedwater tank serves multiple needs. It is used as a hot condensate receiver, cold water makeup addition point, feedwater heating vessel, deaerator, hot feedwater storage reservoir, and feedpoint for various chemical treatments.

The design and construction of feedwater tanks is often poorly done by people with inadequate training or experience. Bad design and poor operational practices lead to a number of problems, especially corrosion. Some poor design and operating practices include:

- There is no supplementary form of heating provided to the tank, so temperature varies depending on percent condensate return.

- The feedwater tank receives minimal condensate return and is cold.
- The oxygen scavenger cannot cope with the high volume of cold feedwater, and chemical deaeration is poor.
- The feedwater tank is undersized, and oxygen scavenger contact time is limited.
- Catalyzed oxygen scavenger is fed in conjunction with phosphates, chelants, or polymers, which consume the catalyst and thus decrease reaction rate.
- The scavenger feedpoint does not provide good mixing or distribution throughout the tank, contact time is limited, and scavenger consumption is higher than expected.
- Short-circuiting between the cold makeup inlet and the feedwater outlet reduce scavenger contact time.

Boiler systems relying on such poorly designed or operated feedwater tanks suffer rapid and extensive oxygen corrosion in the feedwater tank, feedwater line, boiler (firetube or hot water), steam condensate equipment, and condensate return system. With poor oxygen removal, heavy pitting and tuberculation are often found on the boiler tubes and at the waterline of the feedwater tank and boiler shell.

Figure 10.14 shows a well-designed feedwater tank. Design considerations for a well-designed feedwater tank should include the following:

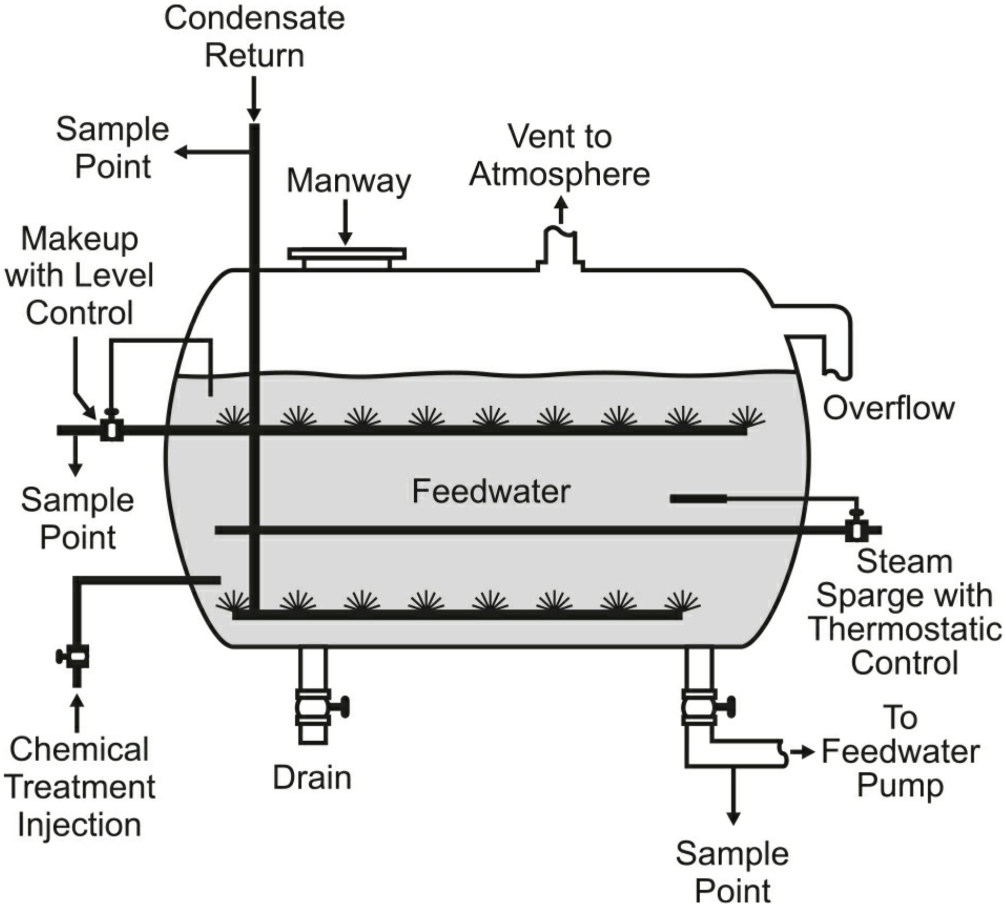


FIGURE 10.14 Properly designed feedwater tank.

- Feedwater tank should be maintained at a constant temperature above 185°F (85°C), ideally above 195°F (91°C), with a supplementary steam sparge, if needed.
- Returned condensate should be discharged through a sparge pipe to the lowest practical point in the feedwater tank. The cold makeup water supply line should also incorporate a sparge pipe but should be positioned at the highest practical point. This arrangement avoids poor water mixing because of stratification.
- The feedwater tank must be adequately vented. Typically, the vent pipe diameter should increase by l inch for every 120 to 150 gal (25 mm for each 0.5 m^3), and two vents are required for tanks larger than 650 gal (2.5 m^3).
- The tank should be large enough to hold a 1-hour supply of feedwater at maximum steaming rate.

- The tank should also be large enough to accommodate peak returns and surges of condensate, as well as shortfalls in makeup water supply caused by softener regeneration problems.
- The tank should be positioned sufficiently high off the floor to ensure that the feedwater pumps are provided with sufficient NPSH, so that they do not cavitate at the desired operating temperature.
- Sample points should be provided for the final feedwater and all sources of water, steam, and condensate that supply the feedwater tank. All feedwater tank sample points should incorporate a sample cooler.

Many manufacturers may not comply with these standards unless required to do so. Even this system with all items as specified will not result in complete removal of all oxygen. However, it will reduce oxygen better than many poorly designed systems in operation today.

Corrosion protection of the tank from oxygen is optional and may consist of baked epoxy linings or stainless steel.

Due to the inefficiency of feedwater tanks in removing dissolved oxygen mechanically, the chemical scavenger used must be catalyzed sodium sulfite. In addition, appropriate alkalinity, pH, time, and temperature conditions must be provided. Product stoichiometry up to five times theoretical may be required. Additional caustic feed may be necessary to counteract the boiler water alkalinity consumption when using liquid bisulfite, which is acidic.

Measuring the desired feedwater or boiler water scavenger residuals never guarantees that all oxygen has been removed. Residual oxygen and scavenger can and do exist together in the system if scavenging conditions are not optimal. Since oxygen is extremely volatile, any dissolved oxygen entering the boiler will release into the steam.

As with deaerators, routine dissolved oxygen testing in the boiler feedwater is critical to assure good corrosion control.

Gas Transfer Membranes

Membranes have been used to degasify water for a number of years in laboratory environments; however, it is only since about 1993 that they have become commercially feasible for industrial systems. The membrane unit design in use today is capable of flow rates up to 400 gpm (91 m^3/h).

Membrane degasification modules are called membrane contactors. They are usually shell-and-tube devices with water on the shell side and gas or vacuum on the tube side. A typical membrane contactor contains thousands of microporous polyolefin hollow fibers (tubes) woven into a fabric array that is wound around a central distribution tube with a central baffle (see Fig. 10.15). Since the membrane is hydrophobic, it will not let the liquid pass through the pores into the gas side. It essentially acts as a support between the gas and liquid phases that allows them to interface at the pores. By adjusting the partial pressure of the gas in contact with the water, gases can be selectively removed (or dissolved) into the water.

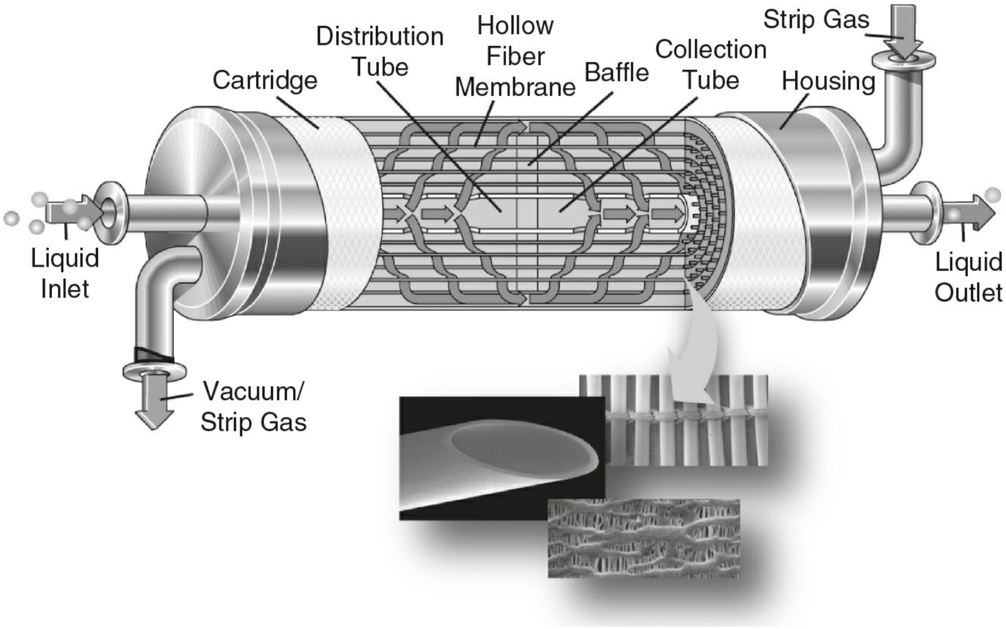


FIGURE 10.15 Liqui-Cel® membrane contactor. (*The illustration of the Liqui-Cel® Extra-Flow Membrane Contactor is provided by Membrana. Liqui-Cel® is a registered trademark of Membrana-Charlotte, A division of Celgard LLC.*)

Water flows radially across the membrane, which induces local turbulence and increases diffusion to the membrane surface in the water phase. Since a membrane contactor contains many small diameter fibers, the interface area between the gas and liquid is very high. In fact, the contact area per unit volume ratio is typically an order of magnitude greater than that for a conventional packed column.

Gas transfer membranes operate with the same principles that govern the operation of a vacuum deaerator or conventional degasification column. If the partial pressure of the gas in contact with the water is reduced, the amount of gas dissolved in the water will be reduced correspondingly. The partial pressure of the gas can be lowered in two ways:

1. The total pressure of the gas phase can be lowered by imposing a vacuum to the gas side of the membrane.
2. The concentration of gases in the gas phase can be altered by using a strip gas that contains little or none of the gas being removed.

Membrane contactors will often use a combination of these two methods to achieve best results. Vacuum requirements may vary with temperature, but 27 inches Hg (686 mm Hg) at 72°F (22°C) is typical.

The degree of oxygen removal varies with temperature and gas evacuation method. Over a range of 55 to 77°F (13–25°C), effluent dissolved oxygen concentration may range from 1.3 to 0.6 mg/L. Typical oxygen removal rates range from 87 to 94% with combined vacuum and nitrogen sweep, falling to 83% with either nitrogen sweep or vacuum alone.

The internal (shell side) pressure drop of a 250 gpm (0.95 m^3/min) contactor operating at maximum capacity is less than 6 psig (41 kPag), allowing these devices to be placed in series for an overall efficiency increase. For example, if three contactors were placed in series and operated under normal conditions, the first contactor would remove 95% of the oxygen, the second contactor would remove 95% of the remaining oxygen, and the third contactor would remove an additional 95% of the remaining oxygen. Starting with 8.5 mg/L O_2 (8500 μg/L), a final dissolved oxygen concentration less than 15 μg/L could be obtained. Up to five contactors can be piped in series to achieve residual oxygen levels below 1 ppb.

The membrane can remove a variety of gases from water, but they must be volatile (present as a dissolved gas), and they must exert a partial pressure. Carbon dioxide is more difficult than oxygen to remove because of its ability to be present in several forms. Only free carbon dioxide (CO_2) is removed, not the bicarbonate (HCO_3^-) or carbonate (CO_3^{-2}) forms.

Carbon dioxide removal may vary from 90% at a pH of 4.9 to 70% at a pH of 5.3. Temperature has a decided effect on carbon dioxide removal with 20 to 60% removal at 54 to 58°F (12–14°C), increasing to 70 to 90% removal at 59 to 75°F (15–24°C). As with oxygen removal, carbon dioxide removal varies with the extraction method. Combined vacuum and nitrogen sweep improves carbon dioxide removal. Even though carbon dioxide removal may be incomplete, the residual CO_2 present in the effluent of a gas membrane contactor will be lower than can be achieved by a forced-draft atmospheric decarbonator. These membrane devices are warranted to 1 ppm of CO_2 while a forced draft atmospheric decarbonator will typically produce effluent water with 7 ppm CO_2.

The membrane contactors have an upper temperature limitation of approximately 140°F (60°C). However, there are fiber variants that can withstand temperatures as high as 185°F (85°C).

Some makeup water treatment plants combine membrane technology with conventional ion exchange polishing or electrodeionization (EDI) technologies. Gas removal is practiced upstream to reduce the ion exchange loading on the anion resin as well as protect the resins from oxidation. Degassed high-purity water can then be stored in lower cost storage tanks, operated with a nitrogen blanket.

The recommended pretreatment ahead of gas transfer membranes to prevent fouling by organics, colloids, and particulates, is filtration down to 10 micron or reverse osmosis (RO). Major components in the operating cost for this system are likely to be membrane maintenance and replacement, along with vacuum pump operation and maintenance.

Activated Carbon Catalysis

The chemical reaction between dissolved oxygen and hydrazine is well known and proceeds very slowly at ambient temperature and neutral pH.

$$N_2H_4 + O_2 \rightarrow 2H_2O + N_2 \tag{10.5}$$

Application of dosages in excess of 300% stoichiometric and contact times over two hours may not result in complete oxygen removal. The use of catalyzed hydrazine, either metallic or organic in nature, at large excess dosages does not increase reaction rates appreciably for low-temperature applications [35–80°F (1.7–27°C)].

A number of patents exist from the mid 1980s for the catalysis of hydrazine and other oxygen scavengers (carbohydrazide, diethylhydroxylamine, and erythorbic acid) by activated carbon. The process involves the addition of scavenger to water, passing the mixture through activated carbon media, followed by ion exchange downstream to remove any impurities added by the carbon bed.

Only the reaction with hydrazine is discussed here, although the other patented scavengers have been used successfully.

Water and hydrazine are intimately mixed before passing through a bed of activated carbon. The reaction is catalyzed by the activated carbon, reaching completion in a matter of seconds and at dosages approaching stoichiometry. Oxygen residuals below 25 μg/L can be obtained, if sufficient contact time is provided in the carbon bed. This typically requires volumetric flow rates less than 2.5 gpm/ft^3 (20 m^3/[h · m^3]). On a continuous basis, flow rates as low as 0.5 to 1 gpm/ft^3 (4–8 m^3/[h · m^3]) may be required. Laboratory data show that influent pH may also be important; however, commercial experience contradicts this with low oxygen effluent obtained within the operating pH range of 5.5 to 10.

Theoretically, there is no need to overfeed hydrazine since the activated carbon will allow stoichiometric reaction. In practice, however, a 10 to 20% hydrazine excess is recommended to allow for small changes in flow rates, dissolved oxygen content, and pumping inaccuracy. The stoichiometric ratio of hydrazine to oxygen is 1:1 on an active weight basis, that is, 1 mg/L active hydrazine should scavenge 1 mg/L O_2 in the presence of activated carbon.

Special grades of activated carbon are not apparently needed, but finer particles provide more surface area for the catalytic reaction than do coarser particles. Care must be taken to avoid particles and grades of carbon that can be lost during backwash.

There are many types of activated carbon, which may be petroleum based or made from materials such as coconut shells. The ash content of such carbons varies considerably, and the industrial and commercial demand for activated carbon sometimes causes extreme shortages of low-ash carbon. However, even low-ash carbon leaches undesirable impurities into the deoxygenated water. With some carbon materials, leaching declines slowly but in others continues at high concentrations for considerable time. When carbon must be replaced, it is frequently found the original low-ash material is not available, and substitute carbon may leach much higher contaminants.

For these reasons, this process must precede polishing treatment such as demineralization for removal of the ionic salt leachates and carbon fines. The amount of silica leached from the carbon may be significant and may require a downstream strong-base anion resin in the hydroxide form for removal. In most instances, a properly regenerated mixed-bed system downstream of the activated carbon media has been sufficient to deal with the leachables.

Lastly, care must be exercised in the design of a storage system that eliminates possible contamination of the effluent after deoxygenation. A floating bladder and nitrogen blanket systems are common approaches.

Ion Exchange Resin Catalysis

This system is often referred to as the catalytic oxygen removal system or CORS. It is similar in many respects to the activated carbon system described previously.

One version of this process uses a palladium coated, strong-base anion exchange resin as the catalyst and hydrogen or hydrazine to react with the oxygen. Residual oxygen in the deoxygenated water can be less than 2 µg/L with stoichiometric dosage of chemical.

This process has also been successfully tested using either hydroxide form strong-base anion resin or anion rich mixed-bed demineralizers with hydrazine or carbohydrazide for the chemical scavenger. Chemical dosage requirements may be two to three times the stoichiometric amount required for the oxygen concentration.

If hydrazine is used, the anion resin need not be regenerated unless other contaminants are present in the water. If carbohydrazide is used, periodic regeneration may be required, because the reaction of carbohydrazide with oxygen produces carbon dioxide that will be removed by the anion resin. In addition, excess hydrazine may be removed using a hydrogen form strong acid cation unit or left in the water to prevent reoxygenation.

Since unit flow rates affect the contact time, they are extremely important to the final oxygen concentration achieved. However, very little data have been published to date for good guidance in this area.

Chemical Oxygen Scavengers

Many pressure deaerators are capable of reducing the oxygen level to less than 10 µg/L. However, considering the corrosive potential of oxygen, it is best to remove all traces of oxygen. This is accomplished with chemical oxygen scavengers that react with the free oxygen to form harmless oxidized products. The reaction products are subsequently removed through boiler blowdown or system venting. Chemical oxygen removal is the last opportunity to prevent oxygen from entering the boiler.

For these scavengers to be effective in protecting the metal surfaces of a boiler system, they must be correctly applied and mixed with the boiler feedwater. The need to protect the system starts at the deaerator or feedwater tank.

Deaerators furnished with separate deaerating vessels mounted on separate storage vessels, have one or more interconnecting legs that act as water downcomers and steam equalizing pipes. In such cases, the preferred scavenger injection point is into the water downcomer between the vessels, using a special injection quill to get maximum mixing. Care must be taken to ensure the water downcomer is used for this purpose and not a steam equalizer.

For units without separate deaerating domes or water downcomers, it is recommended that the scavenger be fed into the storage tank below the water line. A single injection point at either end or into the middle provides poor scavenger and water mixing and often fails to provide sufficient contact time for the reaction with oxygen, especially when equipment stops functioning properly. The recommendation for scavenger feed into the storage section is either to feed into both ends or through a modified header type arrangement that distributes chemical across the entire storage section (see Fig. 10.16).

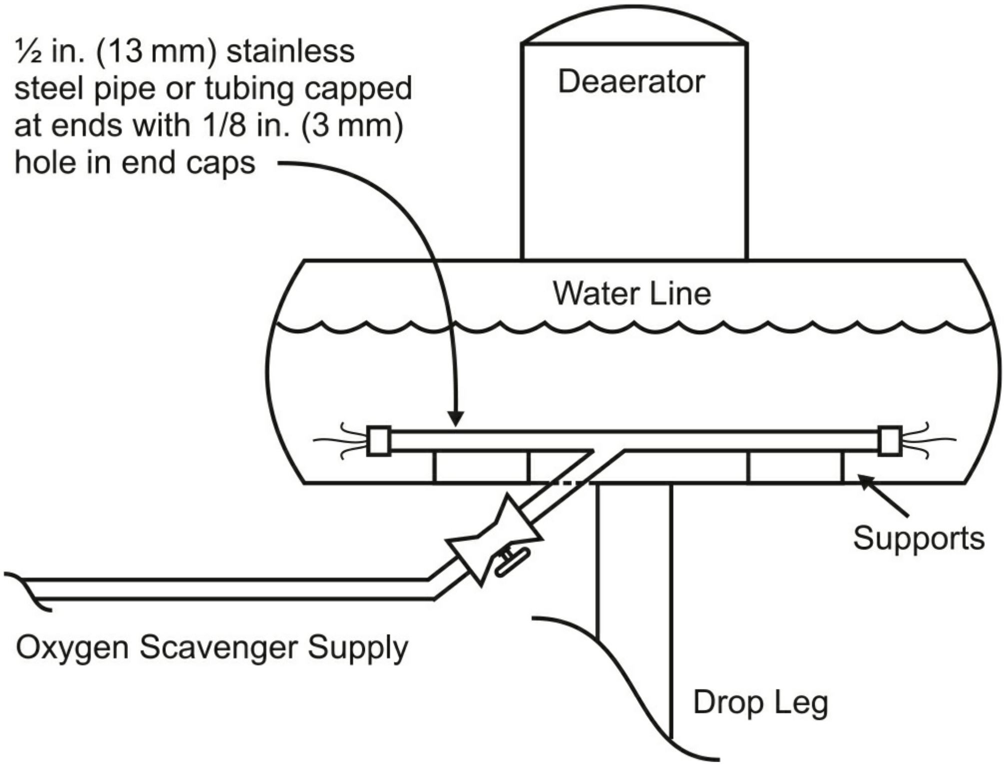


FIGURE 10.16 Alternative oxygen scavenger feed point. The arrow indicates a ½ inch (13 mm) stainless steel pipe or tubing capped at the ends with 1/8 inch (3 mm) hole in the end caps.

There are several commercially available oxygen scavengers in the market place today:

- Sulfite (Na_2SO_3)
- Hydrazine (N_2H_4)
- Carbohydrazide [$(NH_2NH)_2CO$]
- Erythorbate ($RC_6H_6O_6$ where R is H^+, Na^+, or amine)
- Diethylhydroxylamine [$(C_2H_5)_2NOH$]
- Methylethylketoxime (C_4H_8NOH)
- Hydroquinone [$C_6H_4(OH)_2$]

Each scavenger has slightly different characteristics. In actual systems, the effectiveness of oxygen scavengers can depend on many thermodynamic and kinetic factors:

- Scavenger concentration, type, and variability
- Dissolved oxygen concentration and variability
- Time for the chemical reaction
- pH of the water
- Temperature of the water
- Presence of catalysts
- System metallurgy (brass, copper, carbon steel, etc.)
- Other chemical species in the water

Sodium Sulfite (Na_2SO_3)

For many industrial boiler applications, sodium sulfite is an easily controlled oxygen scavenger. Table 10.1 shows typical boiler water sulfite residuals carried at various operating pressures.

Boiler Pressure, psig (MPag)	Sulfite Residual, ppm SO_3^{-2}
up to 150 (1.0)	30–60
150–300 (1.0–2.1)	30–40
300–600 (2.1–4.1)	20–30
600–900 (4.1–6.2)	10–15
above 900 (6.2)	not recommended

TABLE 10.1 Typical Boiler Water Sulfite Residuals at Various Operating Pressures

Sodium sulfite reacts directly with dissolved oxygen.

$$2Na_2SO_3 + O_2 \rightarrow 2Na_2SO_4 \tag{10.6}$$

Approximately 8 mg/L of pure sodium sulfite is required to react with 1 mg/L of dissolved oxygen.

Sodium sulfite can be catalyzed or uncatalyzed. Reaction rates of both catalyzed and ordinary sodium sulfite increase with temperature. Even at typical deaerator outlet temperatures of 210 to 250°F (99–121°C), catalyzed sulfite is preferred to uncatalyzed sulfite for the very short reaction time available in boiler feedwater systems.

Reaction time is an important consideration. The corrosive reaction of oxygen with wetted steel surfaces at feedwater temperatures above 300°F (150°C) will be faster than the reaction between sulfite and oxygen. It is imperative that the oxygen is chemically scavenged before the feedwater reaches high-temperature heaters, economizers, or the boiler metal itself. To avoid releasing corrosive oxygen into the steam, the oxygen must be chemically reduced before the feedwater enters the boiler drum.

Cobalt salt, a commonly used catalyst, speeds the reaction of sulfite at low temperatures. A drawback is that this catalyst can be deactivated or precipitated by the presence of phosphates, phosphonates, chelates, polymers, or solutions of pH 9 or higher.

Following are some disadvantages associated with using sodium sulfite:

- Sodium sulfite adds solids to the boiler water. This may contribute to an increased blowdown requirement. Blowdown is a direct loss of energy and increased water treatment costs.
- Sodium sulfite cannot be used in spray attemperation applications, because the solids contribution of sodium sulfite would cause superheater and turbine deposits. In addition, since sodium sulfite must be fed after the attemperation take-off point, all equipment upstream of that point would be subject to oxygen corrosion and costly repairs unless stainless steel is used. Additionally, when feeding sulfite after the attemperation water take-off, the available reaction time between the oxygen and the scavenger is greatly reduced.
- The decomposition of sulfite to corrosive gasses of hydrogen sulfide (H_2S) and sulfur dioxide (SO_2) begins at a pressure of approximately 600 psig (4.1 MPag). For this reason, the use of sulfite as an oxygen scavenger is not recommended above 900 psig (6.2 MPag).
- Sodium sulfite acts primarily as an oxygen scavenger; it is not generally recognized as a metal passivating agent.
- Overfeed or high dosages of liquid sodium bisulfite can result in acidic conditions in both the feedwater and boiler equipment. This most commonly occurs with a malfunctioning deaerator, when the tendency is to continuously increase scavenger feed in the attempt to

maintain a residual.

Additionally, sodium sulfite (or liquid sodium bisulfite) is not recommended for the following applications:

- Boiler systems using coordinated phosphate programs
- Condensate systems (sulfite is not volatile and will add solids to the condensate)
- Lay-up or cold storage of nondrainable superheaters (sulfite will add solids to the water, resulting in superheater deposits)

The use of sulfite as a feedwater oxygen scavenger is an industry-wide practice that generally does not cause problems when used under established guidelines. However, if the dissolved oxygen is high and an insufficient amount of sulfite is fed to react with all of the oxygen, the presence of sulfite in highly oxygenated water can exacerbate pitting.

Hydrazine (N_2H_4)

Hydrazine can be used at all operating pressures and where feedwater is used for steam attemperation. Hydrazine reacts directly with oxygen.

$$N_2H_4 + O_2 \rightarrow 2H_2O + N_2 \qquad (10.7)$$

The direct reaction with oxygen proceeds relatively slowly at temperatures below 300°F (150°C). However, the rate is highly sensitive to the presence of both homogeneous (soluble) and heterogeneous (insoluble) catalysts. For example, the reaction of hydrazine with oxygen can proceed at an acceptable rate at temperatures as low as 150°F (65.6°C) in the presence of heterogeneous catalysts such as the surface of mild steel or copper. A proposed mechanism for this catalysis utilizes the following overall reactions:

$$4Fe_3O_4 + O_2 \rightarrow 6Fe_2O_3 \qquad (10.8)$$

$$6Fe_2O_3 + N_2H_4 \rightarrow 4Fe_3O_4 + 2H_2O + N_2 \qquad (10.9)$$

In the presence of copper or its alloys, the reactions proceed as follows:

$$2Cu_2O + O_2 \rightarrow 4CuO \qquad (10.10)$$

$$4CuO + N_2H_4 \rightarrow 2Cu_2O + 2H_2O + N_2 \qquad (10.11)$$

At boiler water or steam temperatures above 400°F (204°C), hydrazine begins to decompose to form ammonia, nitrogen, and sometimes hydrogen by either or both of Eqs. 10.12 and 10.13. By 600°F (316°C), hydrazine is virtually gone.

$$3N_2H_4 + \text{heat} \rightarrow 4NH_3 + N_2 \qquad (10.12)$$

$$N_2H_4 + \text{heat} \rightarrow N_2 + 2H_2 \qquad (10.13)$$

Hydrazine also enhances metal passivation.

Some hydrazine products are available in the catalyzed form. Tests have shown that catalyzed hydrazine is a more effective oxygen scavenger at temperatures well below those found in feedwater and boiler systems, but shows no significant advantages at elevated temperatures.

Hydrazine also has drawbacks:

- One of the decomposition products of hydrazine is ammonia (NH_3). Ammonia will increase the corrosion rates of copper and copper alloys in the presence of oxygen.
- Hydrazine is a suspect human carcinogen; therefore, it should be handled with the least exposure possible. Closed feeding systems should be used to eliminate exposure. Studies have shown that when hydrazine is handled in closed or ventilated systems, the levels can be controlled to less than 0.1 mg/L in air.
- At low temperatures, hydrazine is slow to react. If, as in some utilities, hydrazine is fed to the condensate hotwell, very high dosages are necessary to protect the system fully. Slow reaction time means the possibility of oxygen attack, even with hydrazine in the system.

Carbohydrazide [$(NH_2NH)_2CO$]

The concerns associated with handling hydrazine prompted the development of an alternative. The product developed, carbohydrazide, can be used in all types of boilers. Although it is not volatile, all of its decomposition, hydrolysis, and reaction products are, so carbohydrazide is often referred to as an all-volatile chemistry.

The reaction of carbohydrazide with oxygen is similar to that of hydrazine but more complex. Carbohydrazide treatment provides numerous intermediary reactions that increase the reactivity of the product and can provide improved metal passivation. At temperatures below 275°F (135°C), carbohydrazide reacts directly with oxygen.

$$(NH_2NH)_2CO + 2O_2 \rightarrow 2N_2 + 3H_2O + CO_2 \qquad (10.14)$$

This makes carbohydrazide a useful oxygen scavenger as well as metal passivator for feedwater systems (deaerators, economizers, etc.).

At temperatures above 275°F (135°C), carbohydrazide begins to hydrolyze to form hydrazine and carbon dioxide (CO_2).

$$(NH_2NH)_2CO + H_2O \rightarrow 2N_2H_4 + CO_2 \qquad (10.15)$$

As the temperature increases further, the hydrazine formed from the carbohydrazide decomposes, as discussed earlier.

Carbohydrazide is unique because one of the breakdown products is hydrazine. This means that at higher temperatures, carbohydrazide continues to scavenge oxygen and passivate metal surfaces. Above 400°F (204°C), hydrazine begins to decompose to ammonia, nitrogen, and water, none of which adds significant conductivity to the boiler water.

Erythorbate ($RC_6H_6O_6$ Where R Is H+, Na+, or Amine)

The erythorbate-based oxygen scavenger is a nonvolatile organic chemical reducing agent designed to scavenge oxygen and enhance passivation of metal surfaces. Similar to L-ascorbic acid (vitamin C), D-erythorbic acid has been used since 1980 as a boiler water oxygen scavenger. Typically, erythorbic acid is neutralized with either an amine or sodium hydroxide. Where the acid is neutralized with amine, the product may be used in boiler feedwater used for steam attemperation, because the product decomposes to gases at elevated temperatures. Where the acid is neutralized with caustic, the product should not be used in attemperation water, because the sodium salts will deposit on superheater tubes and turbine blades. Figure 10.17 shows the chemical structure of these compounds.

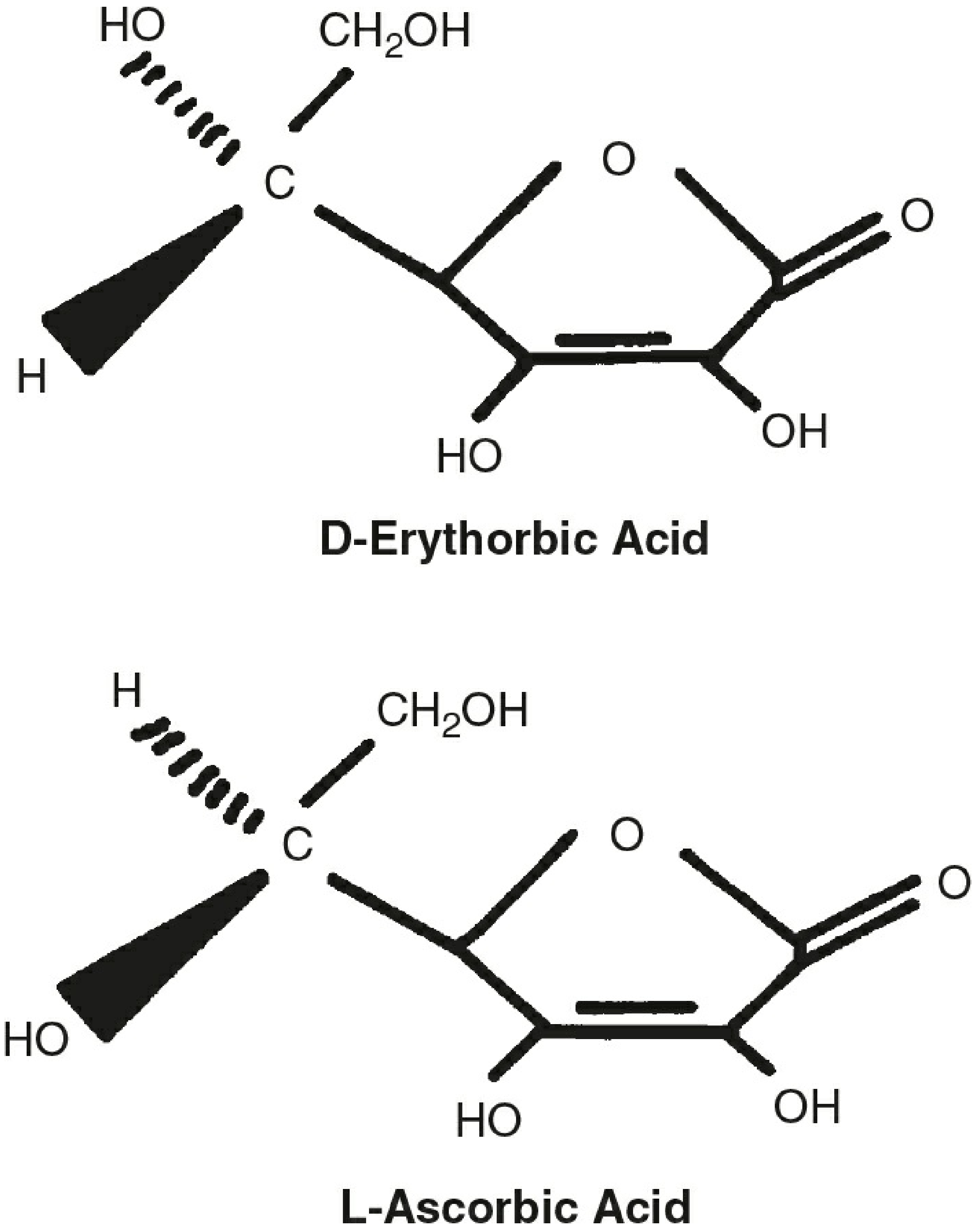


FIGURE 10.17 Chemical structures of D-erythorbic acid and L-ascorbic acid.

The reaction of erythorbate with dissolved oxygen is complex, and the complete mechanism is not yet known. However, the overall reaction occurs as follows (R represents the preferred amine form):

$$RC_6H_6O_6 + \frac{1}{2}O_2 \rightarrow RC_6H_4O_6 + H_2O \qquad (10.16)$$

Erythorbate does not contribute solids to boiler water. At elevated temperatures [500°F (260°C)], erythorbate decomposes to CO_2 and water.

Amine-neutralized erythorbate can be used for spray attemperation, because it breaks down to the volatile components of carbon dioxide and water under attemperation conditions. Field studies demonstrate that erythorbic acid does not contribute to turbine deposits. The unique chemistry of erythorbate permits it to be added upstream of the spray attemperation take-off point. Because it can be added at an earlier point in the feedwater system, more of the equipment can be protected from oxygen attack.

Because erythorbate begins to thermally decompose at deaerator temperatures, overfeed or relatively high dosages can result in acidic conditions in both the feedwater and boiler equipment. This most commonly occurs with a malfunctioning deaerator, when the tendency is to continuously increase scavenger feed in the attempt to maintain a residual.

Diethylhydroxylamine [$(C_2H_5)_2NOH$]

Diethylhydroxylamine (DEHA) has been used in boiler water treatment since 1981. DEHA is both an oxygen scavenger and a metal passivator. However, Nalco research suggests hydrazine, carbohydrazide, and erythorbate are better oxygen scavengers, reductants, and metal passivators than DEHA.

Being an amine, DEHA acts as a typical neutralizing amine ($pK_a = 8.3$). In systems using DEHA, the neutralizing amine feed rate can often be reduced. DEHA has a volatility distribution ratio similar to that of many neutralizing amines. Since it is volatile, DEHA can be fed to the preboiler system and provide protection throughout the entire boiler system, including the condensate system. DEHA does not add solids to water; therefore, DEHA can be used in steam attemperation water. Its amine characteristics (basicity and volatility) are among the most attractive features of DEHA.

The reaction of DEHA with dissolved oxygen is complex and appears to generate intermediates, which are further oxidized at higher temperatures. The reaction rate is dependent on pH, temperature, and the ratio of DEHA to dissolved oxygen. Theoretically, DEHA reacts with oxygen as follows:

$$4(C_2H_5)_2NOH + 9O_2 \rightarrow 8CH_3COOH + 2N_2 + 6H_2O \qquad (10.17)$$

In practice, the reaction does not proceed stoichiometrically to acetic acid as shown in Eq. (10.17). The first-stage reaction is believed to produce a nitrone as shown in Eq. (10.18).

$$(C_2H_5)_2NOH + \tfrac{1}{2}O_2 \rightarrow C_2H_5NOCH_3CH + H_2O \qquad (10.18)$$

The nitrone is further oxidized to acetaldoxime as shown in Eq. (10.19).

$$C_2H_5NOCH_3CH + \tfrac{1}{2}O_2 \rightarrow CH_3CHNOH + CH_3CHO \qquad (10.19)$$

When sodium hydroxide is present in the boiler water, the acetic acid produced is trapped as sodium acetate and removed by continuous blowdown. The other reaction products are volatile and exit the boiler with the steam. The autodecomposition temperature for DEHA starts at 255°F (124°C), and by 400°F (204°C), there is no DEHA remaining. In systems with superheat, additional DEHA might be needed after the superheater to assure complete protection.

As an organic compound, DEHA has the potential to cause the same acidic problems in feedwater and boiler equipment due to overfeed or high dosages as erythorbate, methylethylketoxime, and hydroquinone. This most commonly occurs with a malfunctioning deaerator, when the tendency is to continuously increase scavenger feed in the attempt to maintain a residual.

DEHA quickly degrades as the pressure increases above 240 psig (1.7 MPag). The major degradation product appears to be diethylamine, a volatile neutralizing amine that will contribute to pH control in the steam condensate system. Some ammonia may also be formed.

DEHA will react with iron and copper oxides to form passive metal films as shown in Eqs. 10.20 and 10.21.

$$(C_2H_5)_2NOH + 6Fe_2O_3 \rightarrow 4Fe_3O_4 + CH_3CHNOH + CH_3CHO + H_2O \qquad (10.20)$$

$$(C_2H_5)_2NOH + 4CuO \rightarrow 2Cu_2O + CH_3CHNOH + CH_3CHO + H_2O \qquad (10.21)$$

In commercial products, DEHA is generally blended with other materials.

In oxygen scavenger formulations, DEHA is typically blended with hydroquinone, which improves oxygen scavenging at low temperatures. In condensate system formulations, DEHA can be blended with various neutralizing amines.

Methylethylketoxime (C_4H_8NOH)

Methylethylketoxime (MEKO) was patented as an oxygen scavenger in boiler systems in 1984. The reaction with oxygen is virtually nonexistent at room temperature without a catalyst and is independent of solution pH, which is unusual for an oxygen scavenger. The reaction of MEKO with oxygen produces only volatile reaction products [methylethylketone (MEK), nitrous oxide, and water] as shown in Eq. (10.22).

$$2CH_3CH_3CH_2CNOH + O_2 \rightarrow 2CH_3CH_3CH_2CO + N_2O + H_2O \tag{10.22}$$

Above 572°F (300°C), MEKO decomposes to MEK, nitrous oxide, nitrogen, ammonia, and carbon dioxide. Since all of these materials are volatile, MEKO can be used in steam attemperation water.

Like DEHA, MEKO is volatile and protects the postboiler system when fed to the preboiler equipment. However, in systems with superheaters, additional MEKO should be added after the superheaters to assure complete coverage and protection. MEKO has a volatility distribution ratio between that of diethylaminoethanol and cyclohexylamine.

Proponents of MEKO claim it reacts with iron and copper oxides to form passive metal films. The suggested pathways are shown in Eqs. 10.23 and 10.24.

$$2CH_3CH_3CH_2CNOH+6Fe_2O_3 \rightarrow 4Fe_3O_4+2CH_3CH_3CH_2CO+N_2O+H_2O \tag{10.23}$$

$$2CH_3CH_3CH_2CNOH + 4CuO \rightarrow 2Cu_2O + 2CH_3CH_3CH_2CO + N_2O + H_2O \tag{10.24}$$

As MEKO reacts and degrades, it generates ammonia. At 1800 psig (12.4

MPag), MEKO will produce the same amount of ammonia as would be generated from an equivalent amount of nitrogen in the form of hydrazine.

Literature shows that MEKO does not always react with oxygen to completion, even in the presence of copper, and the reaction may be only 60 to 70% complete. MEKO, like DEHA, is a slow oxygen scavenger at low temperatures. The hydrolysis of MEKO to hydroxylamine produces the scavenging ability noted for this compound. At temperatures above 385°F (196°C), MEKO decomposes to organic acids and other species that have little or no value as oxygen scavengers.

In electric utility systems, MEKO and DEHA feed points are often to the shell side of the feedwater heaters. This is done to enhance scavenging (heat activation) due to the negligible scavenging by these chemistries at low temperatures.

Like erythorbate, DEHA, and hydroquinone, MEKO has the potential to cause acidic problems in both feedwater and boiler equipment due to overfeed or high dosages. This most commonly occurs with a malfunctioning deaerator, when the tendency is to continuously increase scavenger feed in the attempt to maintain a residual.

Hydroquinone [$C_6H_4(OH)_2$]

Hydroquinone (HQ) was first used in boiler water applications as an additive in hydrazine solutions, forming “catalyzed” hydrazine. Today, products can be found using HQ alone. HQ is also used in DEHA formulations to provide better oxygen scavenging at low temperatures.

The reaction rate between HQ and dissolved oxygen is dependent on temperature, solution pH, and the ratio of HQ to dissolved oxygen. The reaction proceeds quite vigorously even at low temperatures, which is why HQ is often used to enhance other oxygen scavengers. The HQ-oxygen reaction is quite complex and appears to involve multiple stages. Based on autoclave studies, the first-stage reaction is believed to yield benzoquinone as shown in Eq. (10.25).

$$C_6H_4(OH)_2 + \frac{1}{2}O_2 \rightarrow C_6H_4O_2 + H_2O \qquad (10.25)$$

The benzoquinone subsequently undergoes further reaction with dissolved oxygen to yield light alcohols and ketones as shown in Eq. (10.26).

$$C_6H_4O_2 + O_2 \rightarrow \text{light alcohols} + \text{ketones} + CO_2 \qquad (10.26)$$

Due to the secondary reaction [Eq. (10.26)], less than stoichiometric amounts of HQ are needed to successfully scavenge dissolved oxygen in boiler feedwater. Because the amount of HQ used in typical applications is small, the amount of reaction products is very low.

The reaction products between HQ and dissolved oxygen do not add solids to water; therefore, HQ can be used in attemperation applications.

In some low-pressure, high-purity boiler water applications, HQ can depress the boiler water pH below the desired set point. Neutralizing amines might not raise the boiler water pH, because the amines are volatile while HQ is not. In high-pressure applications, HQ is volatile and behaves like DEHA and MEKO, protecting the postboiler system.

HQ contains no nitrogen; therefore, HQ does not generate any ammonia.

Proponents of HQ claim it will passivate iron and copper oxides; however, the exact reactions are not fully understood.

One of the major drawbacks of hydroquinone is its toxicity; it is listed as a mutagenic and Class B poison.

Monitoring and Control

In the early part of the 21st century, steam plant management teams came to face a new series of challenges. The one thing that had not changed was the need to assure continuous steam flow to whatever process the facility needed for production. Moreover, the competitive nature of the global economy made cost-effective steam production even more important. However, other things were definitely changing. Fuel costs were increasing, sometimes rapidly, putting extreme budgetary pressure on utility costs. The workforce was changing, getting older in some cases, much less experienced in others, with headcount reduced at more plants, making previous operating strategies impossible to maintain. Finally, a new level of corporate involvement in plant operations was implemented, to oversee operations that were vital to survival of the parent company.

The boiler feedwater system is a frequently overlooked source of steam plant challenges. Water temperatures are not so high as to drive chemical reactions to instantaneous completion, but they are certainly accelerated over ambient conditions. Considering the boiler economizer as part of this system, fireside temperatures are not so high as to cause short-term or even long-term overheat failures. However, mechanical stresses cause a disproportionate amount of forced downtime. In addition, safety must be considered. Corrosion failure of a feedwater line can cause explosive release of water and steam into the surrounding work areas, and fatalities have resulted from these events. Therefore, the need for improvement in the operation, control, and maintenance of the boiler feedwater system is clear.

Previous operating strategies focused on maintaining boiler feedwater pH and dissolved oxygen concentration to maintain reliable system operation. Details of this are more fully described earlier in this chapter, but are focused on collecting a cooled sample of feedwater and using instruments to measure pH and oxygen and scavenger concentration. This type of measurement presents several problems when attempting to maintain on-line control. First and simplest, the process of sample cooling necessarily induces a lag time between when the sample was extracted from the feedwater line and when it is analyzed. In the case of an excursion or process event, this lag or delay can allow some period when the system is not controlled. Secondly, because the target for the desired dissolved oxygen concentration in boiler feedwater is 10 μg/L or less, any air intrusion into the sample could be interpreted as an excursion. The oxygen concentration in air is about 20%, while the desired concentration in feedwater is less than 10 μg/L. Therefore, even a very small influx of air during sampling is enough to suggest a serious event, when one is not actually occurring.

A new corrosion monitoring and control technology called AT ORP^{TM} (At-Temperature Oxidation/Reduction Potential) has been developed to overcome weaknesses of previous tools. This online monitoring tool can minimize corrosion in industrial and utility boiler systems by measuring the net oxidation/reduction potential (ORP) of the hot water at actual feedwater operating temperatures and pressures. This eliminates both sample lag time concerns and potential for air intrusion as the sample is cooled, because the sample is never cooled for analysis. This technology detects subtle changes in oxidation/reduction stress, and responds in real-time by changing oxygen scavenger or passivator chemical feed to maintain a previously selected ORP set point. This makes it possible to detect and react to conditions inside the boiler system under actual operating temperatures and pressures, allowing the program to deliver superior boiler corrosion control. As part of a larger automation package, at temperature ORP provides continuous corrosion control and represents a paradigm shift in system monitoring and control.

Background

Reaction of oxygen with materials of construction used in boilers is the cause of many corrosion phenomena. This complex process depends on more than just the concentration of oxygen present, but also on factors such as water chemistry and metallurgy. For example, the presence of other chemical species in water could turn oxygen into a more aggressive corrodent. Other important factors include temperature, pressure, fluid velocities, and operational practices. While oxygen is often the primary or essential component in the corrosion process, it might not be the only one.

The conventional method to reduce oxygen corrosion in all industrial and even most utility water systems is to remove molecular dissolved oxygen by mechanical and chemical means. In a very few high-pressure boilers in electrical generating stations that use ultra high-purity water, a different approach has been taken. No oxygen scavenger is used, and in fact, small concentrations of oxygen are deliberately added to the feedwater. In this case, oxygen is used as an oxidant and acts as a passivating agent for carbon steel under carefully controlled conditions. More widely seen in Europe than North America.

Traditionally, the amount of oxygen scavenger fed to boiler feedwater has been based on knowing the amount of dissolved oxygen in feedwater plus some excess amount of scavenger. The amount of excess scavenger fed is based on the desired residual scavenger concentration in boiler feedwater or in boiler water itself. When the scavenger is sodium sulfite, boiler water residual is measured, because sulfite cannot be reliably detected at concentrations less than 5 mg/L, which it would be if a feedwater sample were analyzed. The non-sulfite group of scavengers, including carbohydrazide, ascorbic acid, DEHA, hydroquinone, and methylethylketoxime, are measured in boiler feedwater in the range of 100 µg/L or greater.

It is preferable that the operator knows the feedwater dissolved oxygen concentration without scavenger present. This is a way to assess operation of deaerator hardware to assure reliable performance. The dissolved oxygen concentration should be stable, or it should be measured regularly to make necessary chemical dosage changes. In many plants, chemical scavenger residual is the only parameter measured to assure prevention of oxygen corrosion. This can lead to feedwater system corrosion, because even though a scavenger residual is measured that does not mean all oxygen is scavenged in a timely manner. Kinetics of the reaction between low concentrations of oxygen and low concentrations of scavenger are such that complete removal should not be assumed.

Monitoring and Control Tools

Figure 10.18 shows some of the corrosion morphologies seen from oxygen attack. Massive pitting attack was seen while on sulfite treatment (top side). In this case, insufficient sulfite was fed, leaving high dissolved oxygen conditions (>100 µg/L) with sulfate reaction products, which exacerbate localized pitting corrosion.

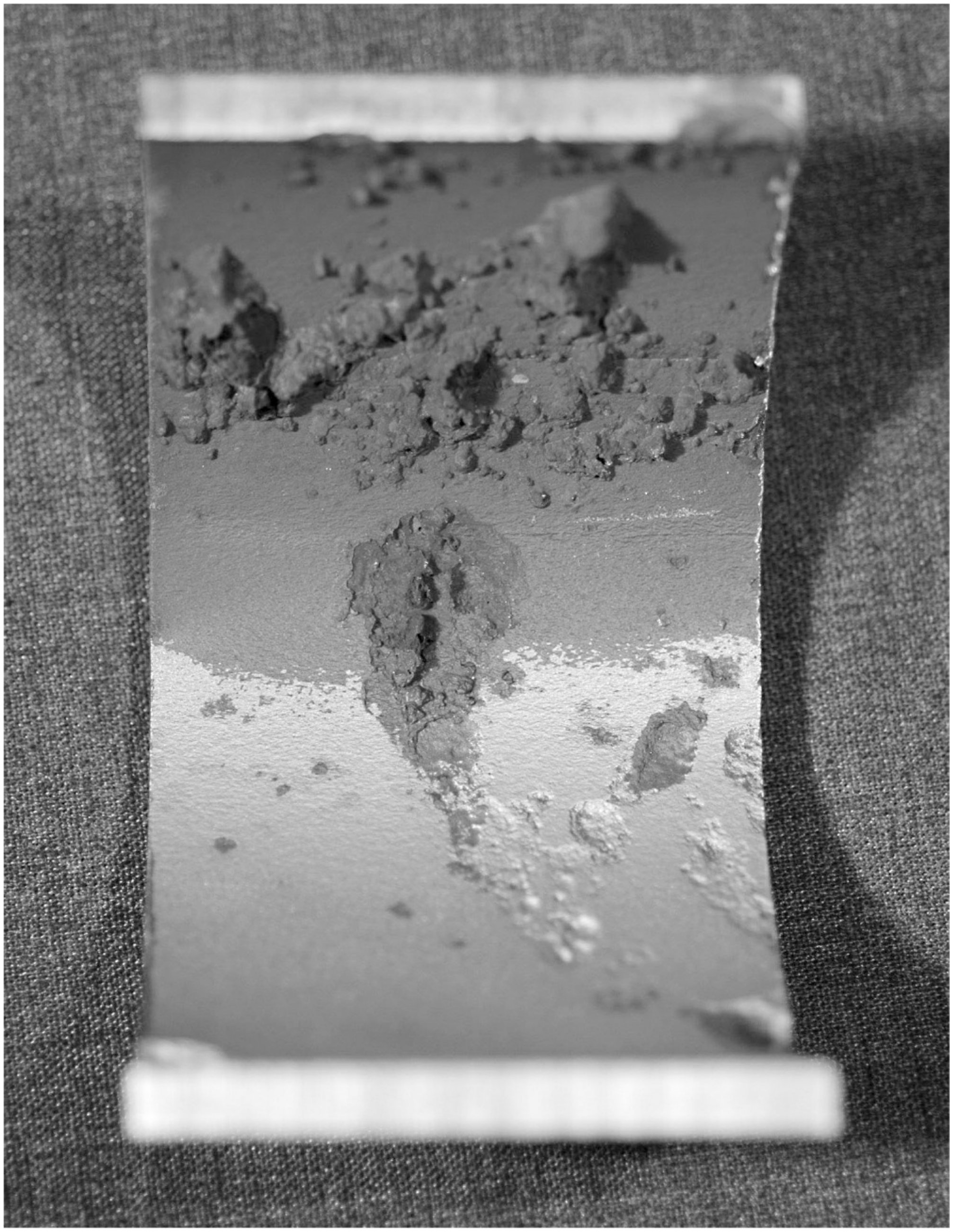


FIGURE 10.18 The top of the sample shows caps of iron oxide (tubercles) covering oxygen pit sites. Often a characteristic red oxide (hematite) is indicative of highly oxidizing conditions. The bottom of the sample shows the localized pitting of mild steel resulting from oxygen-induced corrosion (external corrosion product has been removed).

Performance of combined mechanical and chemical removal processes is often measured continuously using dissolved oxygen probes. Alternatively, dissolved oxygen studies can employ grab sample measurements, where a dye filled ampoule changes color based on oxygen concentration in the sample.

Additionally, color change can be determined spectrophotometrically or with the naked eye through a comparator to correlate to a dissolved oxygen concentration.

Hence, there are several options, varying in sophistication and difficulty of use, to evaluate system performance. It is worth noting that no previous technology really measured conditions of metal surfaces where corrosion actually occurs. Rather, presence or absence of contaminants in the water stream flowing across the metal surface is measured, and the rate of potential damage to the surface inferred from the concentration of contaminant present.

There are various tools for feeding oxygen scavengers/metal passivators. Typical strategies for chemical scavenger feed include:

- Manual pump feed with drawdown calculations and periodic scavenger residual testing.
- Online scavenger residual determinations and control (e.g., online hydrazine analysis).
- Inert TRASAR® feed and control of scavenger products (concentration demand based off inert chemical formulated into product).
- Active TRASAR feed and control of scavenger products (concentration demand based off active chemical formulated into product).
- Feed scavenger off feedwater or steam flow (feed concentration demand).
- Feed chemistry based off timer.
- Slave feed of scavenger to other chemicals being controlled and fed into system or off other mechanical operations (e.g., turning boiler on and off).

Again, none of these feed schemes addresses true demand in real-time in any system, but they have been used with reasonable effectiveness as scavenger feed control schemes. Redox demand measured online at system temperature and pressure has been shown to relate more directly to the driving force or potential for a system to corrode.

Even when some of the best techniques for corrosion monitoring are applied, the very low general corrosion rates seen in boiler systems are difficult to discern. In addition, localized corrosion mechanisms are often occurring, not general corrosion, and the classic electrochemical monitoring tools provide little indication of localized corrosion. Trends in general corrosion can be useful, but are not applicable for use with automated control systems. In situ ORP monitoring overcomes these obstacles and provides a greater understanding of system performance.

Corrosion stresses and their impact on corrosion have been observed to be plant-specific, such as:

- System design and metallurgy
- Dissolved oxygen concentration (incipient and ingress)
- System pH
- Corrosion product concentration
- Temperatures and pressures
- Mechanical configuration and efficiency:
  - Deaerator tray alignment
  - Seal issues
  - Pump issues
  - Deaerator venting
  - Steam supply consistency
  - Condensate storage area integrity
- Seasonal variations in operating profile
- Ratio of condensate return to makeup water
- Changes in feedwater flow and steam load
- Reductant used (if any)
- Presence of specific catalysts to corrosion reactions
- Reductant residence times and concentrations
- Other chemical species (usually pH adjustments)
- Flow effects

While long, even this list is not all-inclusive. Hosts of other possible corrosion stresses exist, and because in situ ORP lends itself to assessing condition of the metal surface, it is the preferred monitoring and control parameter, avoiding need to assess each listed item and all interrelationships.

At-Temperature ORP Monitoring

A different approach from the traditional method of controlling reductants (such as oxygen scavenger feed) is based on redox potential of treated feedwater. ORP values are typically recorded between a noble metal electrode and a reference electrode (often platinum). By measuring redox potential in situ, sample conditioning equipment can be eliminated. Sample system lag times are reduced, and potential for cooling water intrusion into the sample is avoided.

ORP has application wherever corrosion via oxidizing and reducing reactions is of concern. This involves all aqueous corrosion processes. Redox potential of feedwater is a function of dissolved oxygen concentration, oxygen scavenger concentration, and other factors (see Fig. 10.19). Measured ORP directly correlates with potential for systems to corrode. By targeting and maintaining specific redox potential in feedwater, it should be possible to feed the exact dosage of chemical additive required to protect a system from oxygen attack and minimize corrosion rates. The driving force for corrosion can now be controlled in real-time. Scavenger concentration varies based on redox demand. By constantly monitoring feedwater, it is possible to take immediate corrective action when there is a system change. Even in systems that do not feed reductants such as oxygen scavengers, in situ ORP technology still has application due to high sensitivity for detecting changes, which are then assigned to changing mechanical or operational parameters.

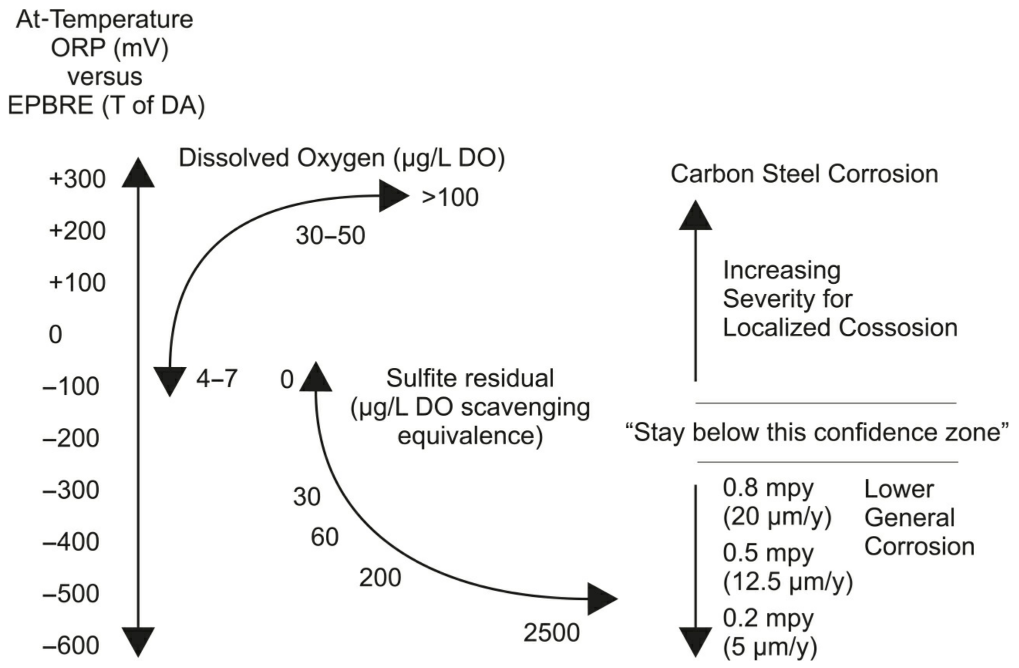


FIGURE 10.19 Schematic ORP correlation with oxygen, sulfite residual, and carbon steel corrosion implications, indicating why this system should be controlled under highly reduced conditions (low ORP zones).

Many feedwater redox stress events are not predictable. Consequently, the majority of redox stress events go undetected, unnoticed, and thus uncorrected. Therefore, controlling redox stress in boiler feedwater is essential to maintaining integrity of boiler systems. Many years of excellent operation can be undone if short-term damaging events occur, especially when they are not detected and proper corrective measures are not taken.

Monitoring ORP has been found to be important in determining presence of electro-active redox species. ORP values reported are the net sum of redox potentials in the sample stream as measured on noble metals such as platinum or gold. It is important to know what potentials are being measured. Simply quoting ORP values without reference to the potential measured and reference electrode used can be very misleading. All conditions for measurement of ORP should be clearly stated, including temperature at which the measurement was taken. All in situ ORP measurements in this chapter were taken using an external pressure balanced reference electrode (EPBRE) filled with 0.1 N potassium chloride (KCl) and a platinum electrode.

ORP values measured against a reference electrode are thus relative numbers and need to be reported as such. Usually, these measurements are made against some standard reference electrode, like a silver/silver chloride electrode filled with potassium chloride. These measurements should be taken under representative conditions of temperature, pressure, and flow.

Flow rates are chosen so that representative water samples pass the electrodes. Ideally, conditions found in the electrochemical cell should mirror those found in bulk water in the system. The goal is to have a sample stream that is flowing “fast enough” to ensure chemical homogeneity of the sample with respect to the system at the point of sampling.

Measuring electrochemical potentials at low temperature and inferring behavior at higher system temperatures is usually misleading. Remembering that corrosion processes in steam systems change dramatically at elevated temperatures, what is of concern is measurement of electrochemical potentials at the system conditions of temperature and pressure.

There are many reasons why it is advantageous to measure ORP at temperature and pressure. Firstly, corrosion occurs in the system at temperature and pressure. Properties of core importance should thus be measured as close as possible to conditions at which critical corrosion processes occur. Active species should not be quenched to low temperature. Correlations at actual operating temperatures and pressures need to be captured. It is possible to see an effect at temperature that cannot be detected at lower temperatures, as equilibria can vary markedly with temperature.

The at-temperature sampling should be done earlier in the sample stream, so that response is rapid and representative of actual feedwater redox state. This is particularly relevant when sample streams can be sent to instrument panels far away from the point of sample extraction.

With oxygen scavengers, it is well known that they are more reactive at elevated temperatures. This is particularly true of many passivating scavengers like hydrazine, carbohydrazide, DEHA, etc. One reason for this is that the power of the reductant is enhanced at temperature, and thus, control based on reductant residual is more sensitive and realistic at temperature.

ORP measurement and control zones can be broadly represented as in Fig. 10.20. “DA + Scav” refers to the majority of systems with a deaerator and an oxygen scavenger/metal passivator. “+Cu” shows that to maintain low corrosion rates of copper alloys (as compared to carbon steel), a different ORP control zone is preferred. “OWT” applies to those systems practicing oxygenated water treatment. These types of systems, where small amounts of oxygen are purposefully added to feedwater systems to lower corrosion rates of iron-based metallurgies, apply only to a few electric utility-based systems.

Systems using all volatile treatment (AVT) without scavenger typically operate at the lower end of OWT zones.

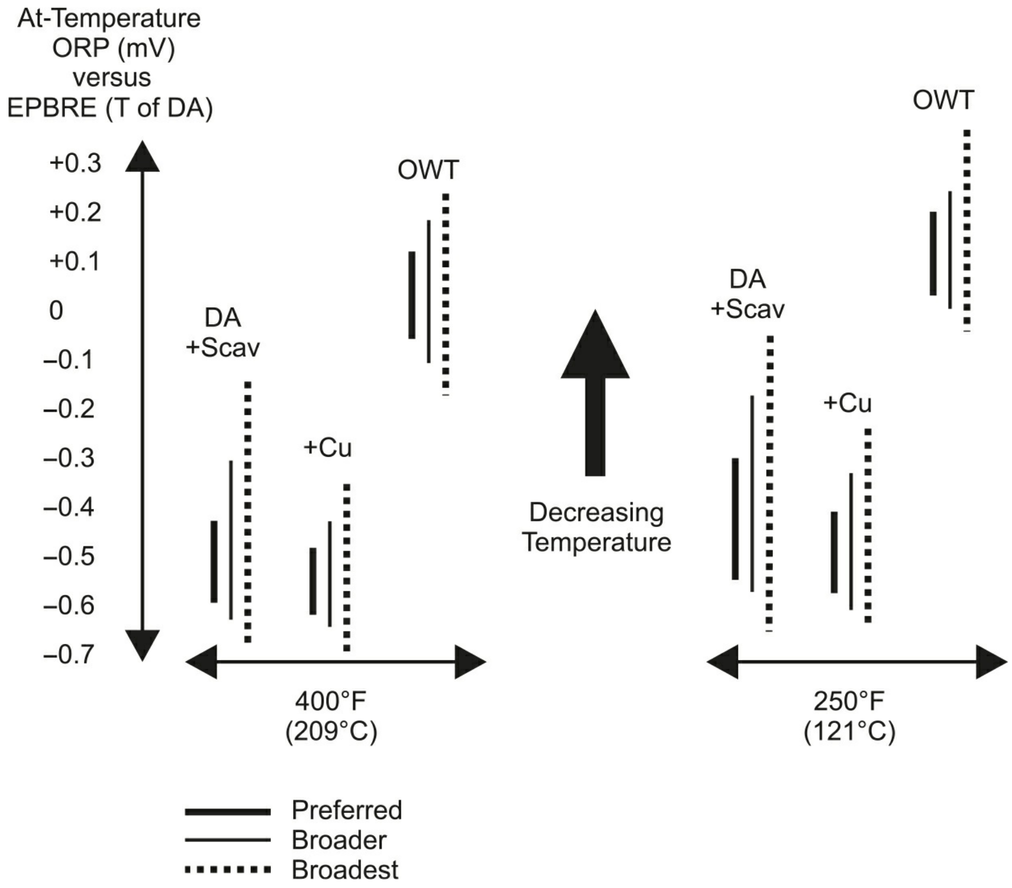


FIGURE 10.20 Examples of ORP control zones in boiler feedwater.

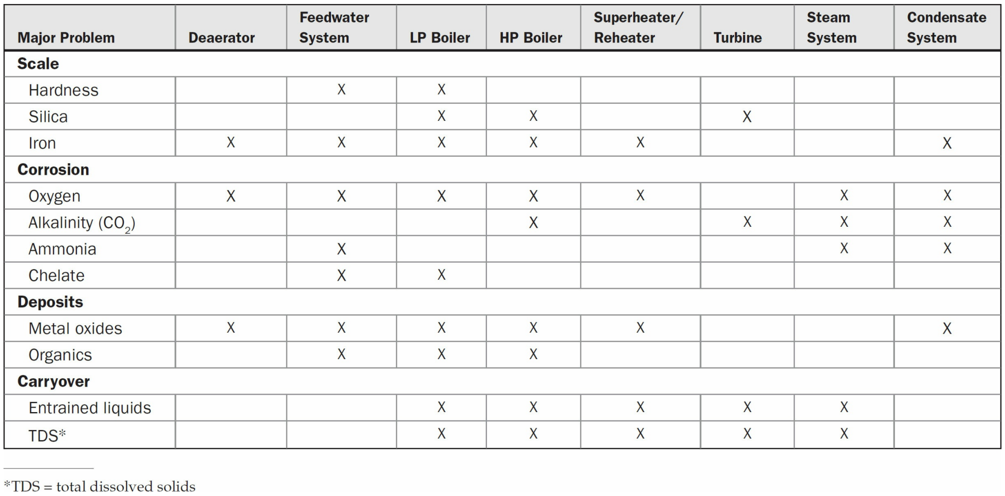
ORP control zones shift slightly more positive as temperature is lowered. Well-operated systems containing sulfite typically reside in the lowest (largest negative number) zones. Weaker reductant use results in higher ORP values. Control zones shift as a function of background dissolved oxygen and pH. Systems tending to have higher background dissolved oxygen values, that tend to be at lower temperatures than systems that operate with conventional pressurized deaerators, operate at higher ORP control zones. The ultimate goal is always real-time system protection using at-temperature ORP in control mode. This leads to plant-specific control zone selection, based on system specifics.

CHAPTER 11

Boiler Feedwater Treatment

The various concepts and practices associated with boiler cycle chemistry will be approached here from a problem and solution standpoint. The boiler cycle is defined as all the contributing components of the system, from the feedwater to the condensate. The pretreatment, deaeration, and treatment chemicals are all used in the cycle to avoid or eliminate problems associated with dissolved or suspended solids and gases in feedwater. These constituents, if left unchecked, may cause considerable damage throughout a steam system.

Table 11.1 illustrates the four major problems associated with boiler systems and where these problems are likely to occur. Chemical treatment must be approached based upon where in the cycle the problems tend to occur. This table is just an approximation and not an absolute. For example, hardness scale is generally not a problem in a high-pressure boiler [1000 psig (6.9 MPag)]; however, if a condenser leak occurs, hardness will be brought back to the boiler through the condensate, and hardness scale will become a significant problem in short order.



Major Problem	Deaerator	Feedwater System	LP Boiler	HP Boiler	Superheater/ Reheater	Turbine	Steam System	Condensate System
Scale								
Hardness		X	X					
Silica			X	X		X		
Iron	X	X	X	X	X			X
Corrosion								
Oxygen	X	X	X	X	X		X	X
Alkalinity (CO_2)				X		X	X	X
Ammonia		X					X	X
Chelate		X	X					
Deposits								
Metal oxides	X	X	X	X	X			X
Organics		X	X	X				
Carryover								
Entrained liquids			X	X	X	X	X	
TDS*			X	X	X	X	X	

*TDS = total dissolved solids

TABLE 11.1 Common Problems and Affected Areas in Boilers

Scale on boiler surfaces can lead to serious problems. Even an extremely thin layer of scale is sufficient to retard heat transfer and reduce boiler efficiency. More importantly, scale can cause the boiler heat transfer surfaces to overheat, leading to failures.

The major step in preventing boiler waterside scale is, the careful control and maintenance of all makeup and feedwater pretreatment systems, to limit the amount of impurities entering the boiler. Proper chemical treatment plays a critical role in scale control and is used to inhibit the deposition of minerals that do make their way into the boiler.

This chapter is primarily concerned with industrial boilers. Chapter 33 on the Power Industry contains a discussion of boiler water treatment for high-pressure utility boilers. Some industrial boilers using high-purity feedwater might also use the boiler water treatments discussed in Chap. 33. The boiler owner/operator in conjunction with the water treatment supplier must determine the correct internal treatment program and boiler water operating limits for each application.

Hardness Scale

The primary reason scale forms is that the solubility of the scale forming salts in water decrease as the temperature and concentrations increase. When feedwater is elevated to boiler water temperature, and the concentration of the scale-forming salts exceeds solubility, the salts precipitate, and scale forms (see Table 11.2).

Compound	Solubility (g/L as $CaCO_3$)	
	32°F (0°C)	212°F (100°C)
Calcium		
Bicarbonate	1.6	decomposes
Carbonate	0.015	0.013
Sulfate	1.29	1.25
Magnesium		
Bicarbonate	37.1	decomposes
Carbonate	0.1	0.075
Sulfate	170	356
Sodium		
Bicarbonate	38.7	decomposes
Carbonate	61.4	290
Chloride	225	243
Hydroxide	370	970
Sulfate	33.6	210

TABLE 11.2 Solubility of Chemical Compounds

Mineral scale formation (the precipitation of calcium and magnesium salts) usually occurs in boiler feedwater systems (economizers, feedwater pumps, and feedwater lines) and in low-pressure boilers [<1000 psig (6.9 MPag)], where no pretreatment or poorly maintained ion exchange softening is used. Mineral scale is normally not found in boiler systems where demineralization is used or in high-pressure, high-purity systems. The exception to this is where there has been an upset condition such as a condenser leak or a process leak, and the condensate is contaminated with hardness.

Scale forms in improperly treated boiler water systems by one or both of the following mechanisms:

1. The precipitation of relatively insoluble feedwater hardness compounds. Calcium carbonate precipitation at the metal surface is one example.

$$Ca(HCO_3)_2 + heat \rightarrow CaCO_3 + H_2O + CO_2 \qquad (11.1)$$

Uninhibited precipitation tends to form hard scale if it occurs at metal surfaces that are subject to heat transfer.

Magnesium silicate is found in low-pressure systems where sufficient amounts of magnesium are present in conjunction with adequate amounts of silicate ions and a deficiency of free hydrate alkalinity.

$$Mg^{+2} + OH^- \rightarrow MgOH^+ \qquad (11.2)$$

$$H_2SiO_3 \rightarrow H^+ + HSiO_3^- \qquad (11.3)$$

$$MgOH^+ + HSiO_3^- \rightarrow MgSiO_3 + H_2O \qquad (11.4)$$

2. The supersaturation or crystallization of dissolved solids such as calcium sulfate ($CaSO_4$) and silica (SiO_2) in water that contacts heat transfer surfaces. The thin viscous film of boiler water immediately adjacent to the heating surface tends to become more concentrated than the main body of boiler water. As the steam bubbles form, they depart from the metal surface, leaving behind a circular deposit. Eventually, the circular formation is completely filled in with scale. This may occur even though the concentration throughout the main body of the solution does not exceed the solubility limits. Even the most soluble sodium salts may deposit if water is allowed to evaporate to dryness due to plugging, poor circulation, or excessive heat transfer rates.

Scale rarely exists in the pure compound form; it is generally found as complex molecules or as a mixture of compounds within any given sample. Table 11.3 lists the various scales commonly found in feedwater and low-pressure boiler systems.

Name	Formula
Acmite	$Na_2O\ Fe_2O_3\ 4SiO_2$
Analcite	$Na_2O\ Al_2O_3\ 4SiO_2\ 2H_2O$
Anhydrite	$CaSO_4$
Aragonite	$CaCO_3$ (gamma form)
Brucite	$Mg(OH)_2$
Calcium hydroxide	$Ca(OH)_2$
Calcite	$CaCO_3$ (beta form)
Copper	Cu
Cuprite	Cu_2O
Ferrous oxide	FeO
Goethite	$Fe_2O_3\ H_2O$ (alpha form)
Gypsum	$CaSO_4\ 2H_2O$
Hematite	Fe_2O_3
Hydroxyapatite	$Ca_{10}(PO_4)_6(OH)_2$
Lizardite (formerly serpentine)	$3MgO\ 2SiO_2\ 2H_2O$
Magnesium hydroxy phosphate	$Mg_3(PO_4)_2\ Mg(OH)_2$
Magnetite	Fe_3O_4
Sodium ferrous phosphate	$NaFePO_4$
Tenorite	CuO
Thenardite	Na_2SO_4
Xonotlite	$5CaO\ 5SiO_2\ H_2O$

TABLE 11.3 Common Constituents Found in Boiler Deposits

Silica Scale

Silica-based deposits are found primarily in lower-pressure systems [<1000 psig (6.9 MPag)], where the pretreatment system is not designed for silica removal, that is, sodium softening, or where the boiler is operated at excessive cycles of concentration. Although uncommon, silica-based deposits can be found in high-pressure systems, where silica leakage through the anion unit(s) has been a problem. Silica-based deposits become more serious as silica increases and hydrate alkalinity decreases.

Silica can form several types of deposits, such as amorphous silica and magnesium silicate. Amorphous silica appears as a smooth glass-like deposit that is very difficult to remove and is generally cleaned with a hydrofluoric acid solvent. Magnesium silicate generally is tan to off-white and has a somewhat rough texture. Although magnesium silicate is easier to remove than amorphous silica, it is still difficult. Both forms of silica have high insulating properties and can result in tube failures in watertube boilers.

Silica, in addition to forming boiler deposits, can vaporize from the boiler and be carried with the saturated steam as silicic acid. When the steam containing vaporous silica performs work and has some of the superheat content reduced such as going through a turbine, the silica precipitates on the metal surfaces causing deposits. This deposit will reduce the efficiency of the turbine and can result in an imbalance of the turbine wheels. Additionally, unlike sodium-based deposits that can be removed with water washing, the silica deposits are very difficult to remove. Selective silica carryover is not a serious problem below 600 psig (4.1 MPag); however, it can become a very serious problem as the pressure increases, particularly above a pressure of 1000 psig (6.9 MPag).

Figure 11.1 shows the relationship of boiler pressure to the maximum permissible concentration of silica in the boiler water in order to maintain less than 20 μg/L of silica in the steam (the typical maximum concentration allowed in the steam supplying steam turbines).

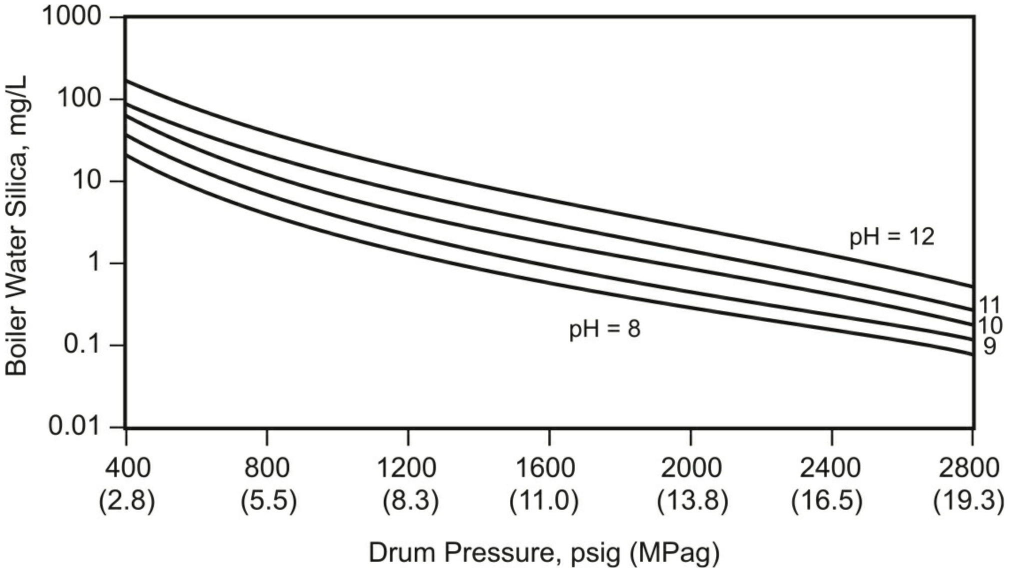


FIGURE 11.1 Effect of drum pressure and pH on allowable silica concentration to maintain steam purity target of 20 μg/L.

Silica control is very important; it can be achieved through proper pretreatment and proper boiler blowdown. In low-pressure boilers using a phosphate-polymer internal treatment program, silica deposition in the boiler can be controlled by maintaining at least a 3:1 ratio of hydrate alkalinity to silica.

Iron Deposits

Iron oxides present in boiler water have caused problems since the dawn of boilers. However, in the beginning, iron deposits were not the major problem or root cause of most boiler failures, as were hardness scale deposits. As the design of boilers evolved from low-pressure, riveted, drum-type boilers, to today's modern high-pressure, high heat flux, thin-walled watertube boilers, the requirement for higher purity boiler feedwater also occurred. The effective removal of calcium and magnesium from boiler feedwater by pretreatment techniques such as lime softening, sodium softening, ion exchange demineralization, and reverse osmosis (RO) has shifted the cause for boiler failures to be predominately due to iron deposits on the heat transfer surface. These deposits cause under-deposit corrosion problems and act as insulators, impairing heat transfer, which can cause the boiler metal to overheat and ultimately fail.

The energy crisis in the early 1970s, caused by the Organization of Oil Exporting Countries (OPEC) oil embargo, had a major impact on industry and the boiler iron story. The loss of cheap energy, and the need to conserve energy, led industry to focus on returning more and more steam condensate as a source of boiler feedwater, due to its valuable energy content and relative high purity. However, the consequence of increasing the amount of returned condensate to the boiler, was the increased amount of iron oxide corrosion products entering the boiler. Most of the corrosion products that deposit in the boiler originate in the steam condensate system. Corrosion of the feedwater piping, economizer, and boiler, as well as the iron entering with the makeup water, are other sources contributing to the boiler iron deposit problem.

The Problem with Iron

Both soluble and insoluble iron (particulate and colloidal) can be present in boiler feedwater and boiler water. Boiler water iron will deposit on the steam generating surfaces of the boiler and cause under-deposit corrosion and overheating problems. Iron deposits on the heat transfer surfaces are typically hard, dense, and porous. The porosity of the deposits allow wick boiling to occur, which provides a mechanism for concentrating and trapping corrosive chemistries such as caustic, acid phosphates, sulfates, and chlorides inside the deposit. In addition, the insulating property of the deposit impairs heat transfer and causes the temperature of the boiler metal to increase.

As shown in Table 11.4, iron oxide deposits are insulating, with hematite deposits being more insulating than magnetite. Note that the values in Table 11.4 do not incorporate the effect of deposit porosity, which varies and affects the actual thermal conductivity. To prevent overheating and rupture of boiler tubes due to the continued buildup of iron deposits, boilers must be acid cleaned periodically.

	Thermal Conductivity	
Compound	**Btu/[h·ft·°F]**	**W/[m·K]**
Calcium phosphate	2.1	3.6
Magnetite	1.7	2.9
Magnesium phosphate	1.2	2.1
Calcium sulfate	0.75	1.3
Lizardite (serpentine)	0.58	1.0
Calcium carbonate	0.53	0.92
Hematite	0.34	0.59
Carbon steel	26.7	46

TABLE 11.4 Thermal Conductivity of Typical Boiler Deposits

Iron Deposition Mechanism

Steam generation in boilers generally occurs under nucleate boiling conditions, where discrete steam bubbles form and break away from the surface, allowing fresh boiler water to reach the surface to cool and clean it and start the process again. Soluble and suspended materials concentrate at the vapor/liquid interface of the bubble (meniscus of the steam bubble) as well as at the point of bubble attachment to the boiler tube. Figure 11.2 is a simple illustration of the growth cycle of a single steam bubble. Deposits occur at the wet/dry interface on the tube surface. The amount of deposit is equal to, or slightly more than, what was contained in the liquid that was vaporized to steam. As the bubble breaks away, fresh liquid sweeps the surface, removing all or some of the solid. Any deposit left behind is eventually baked onto the surface.

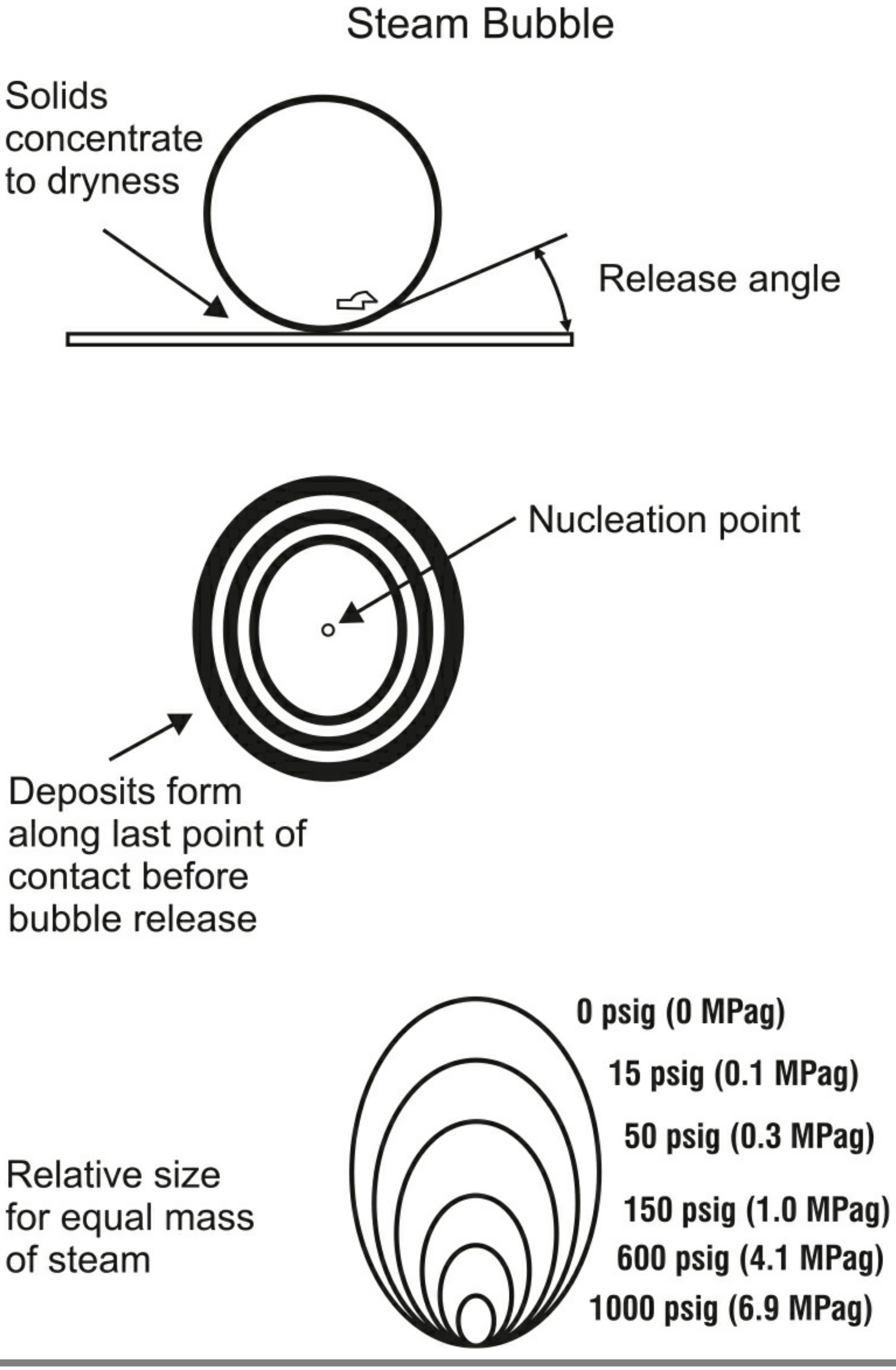


FIGURE 11.2 Steam bubble formation.

Conceptually, Fig. 11.2 is easy to understand. However, the deposition process is far more complicated. A collaborative research project conducted in the mid-1990s by Nalco and Argonne National Laboratory studied the mechanism of iron deposition under nucleate boiling conditions. Factors affecting deposition of iron were found to include pressure, temperature, heat flux, iron concentration, pH, surface roughness (macro and micro), time of bubble attachment, flow rate, and other impurities present in the water.

The research showed that hematite particles tended to agglomerate during the formation, growth, and release of the steam bubble. Interestingly, it was found that the amount of iron deposited on the surface was sixty times more than what is predicted from the simple evaporation to dryness deposition model shown in Fig. 11.2. This finding suggests that there is a complex particle-bubble interaction. It is hypothesized that since the steam vapor inside the bubble is less polar (more hydrophobic) than the boiler water, this causes the hematite particles in the surrounding boiler water adjacent to the bubble to migrate toward and concentrate in the steam bubble meniscus. Then, through capillary and eddy current effects, the iron is drawn down to the surface and deposited at the bubble attachment point.

Heat flux and iron concentration have a significant effect on the deposition rate. The higher the heat flux, the more iron is deposited per unit time. The rate of iron oxide deposition was found to follow first-order kinetics with respect to iron in the boiler water.

Sources of Iron

Iron entering the boiler originates from two main sources:

1. Naturally occurring iron present in the raw water
2. Corrosion of the mild steel components making up the boiler system, including preboiler and post-boiler

Raw water can contain soluble iron salts and particulate/colloidal iron hydroxides and oxides. For instance, well water can contain high levels of soluble iron, which is oxidized to convert the iron to insoluble oxides and hydroxides, to enhance removal during the pretreatment process. In the case of surface water, iron is predominantly present as insoluble iron oxides and hydroxides, because the dissolved oxygen level in the water is sufficient to oxidize the iron and cause its precipitation.

Corrosion of the mild steel components in the pretreatment, feedwater, boiler, and condensate systems is the major source of iron entering the boiler. There are a number of corrosion mechanisms.[1]

Factors affecting mild steel corrosion in boiler systems include pH, temperature, heat flux, dissolved oxygen, carbon dioxide, flow, ionic strength, suspended solids, and boiler treatment chemicals such as chelants and polymers.

Mild steel is used in the construction of boiler systems because of its mechanical strength, high thermal conductivity, and low cost. In addition, mild steel at high temperature under alkaline reducing conditions forms a protective thin adherent magnetite oxide (Fe_3O_4) layer on the surface, which is self-limiting and protects the base metal from the corrosive aqueous environment. Therefore, the recommended pH range for boiler water is 9 to 12 (Fig. 11.3).

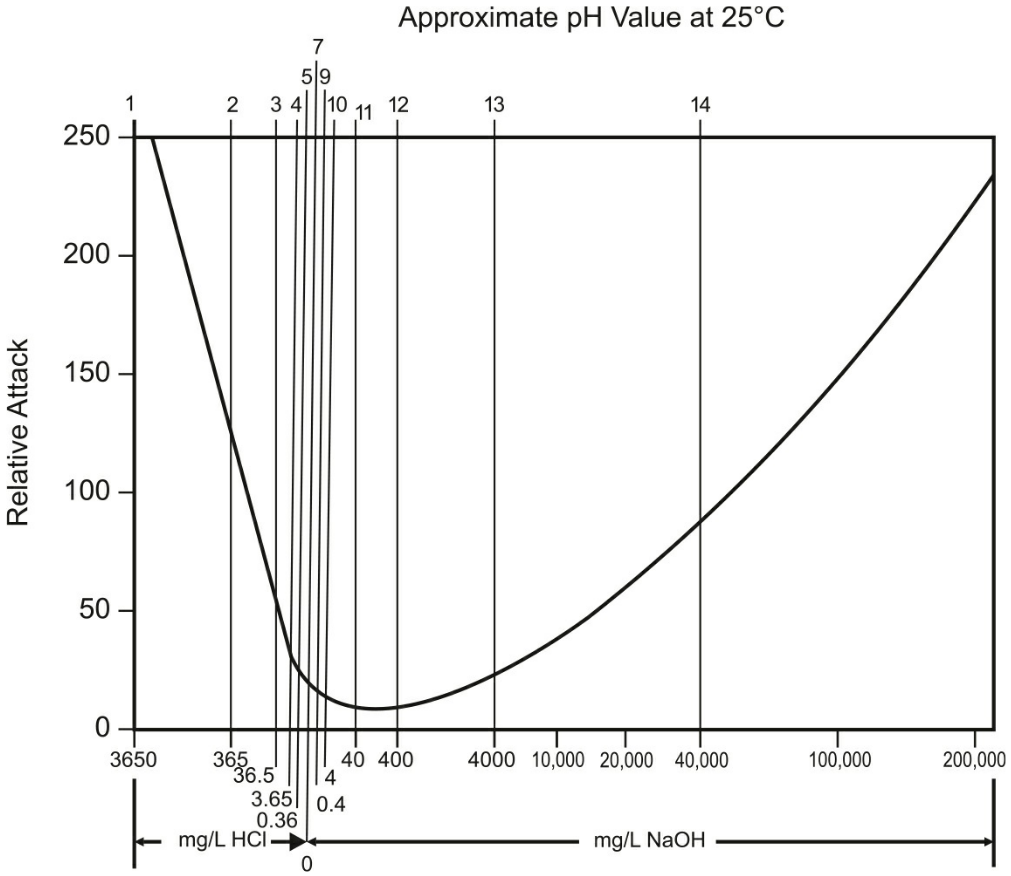


FIGURE 11.3 Relative corrosion rate of boiler steel versus pH and caustic concentration.

The mechanism of magnetite formation, the Schikorr reaction, proceeds through the following steps:

$$Fe + 2H_2O \rightarrow Fe^{+2} + 2OH^- + H_2 \tag{11.5}$$

$$Fe^{+2} + 2OH \rightleftharpoons Fe(OH)_2 \tag{11.6}$$

$$3Fe(OH)_2 \rightarrow Fe_3O_4 + 2H_2O + H_2 \tag{11.7}$$

The formation of ferrous hydroxide [Eq. (11.6)] is the rate-limiting step to the overall production of magnetite, and it is slow below 400°F (204°C). The controlled corrosion process of passivation is achieved as the metal surface goes from an actively corroding state [Eq. (11.5)] to an inactive steady state [Eq. (11.7)]. Since hydrogen is released as the metal becomes passive, hydrogen evolution accompanies the formation of the magnetite film. It has been widely recognized that monitoring hydrogen in the steam of a boiler is an indirect measure of the boiler corrosion activity.

In addition, it should be noted that ferrous ions (Fe^{+2}) are the first product of corrosion [Eq. (11.5)]. Measuring the concentration of Fe^{+2} is an important method to identify active corrosion in boiler systems. Quantifying Fe^{+2} is an important part of the iron control prevention strategy. Any condition leading to the damage of the magnetite protective oxide film will cause an increase in corrosion of the base metal. Mechanical and thermal stresses can fracture the oxide layer creating microcracks, which expose the base metal and allow the corrosion reactions to proceed.

These stresses can eventually lead to exfoliation of portions of the oxide layer, which again exposes the base metal to further corrosion and allows the potential migration of particulate iron to reach the boiler and deposit on the steam generating surfaces. For example, when a paper machine comes back online after being down because of a paper break or some other reason, high levels of suspended iron are initially found in the return condensate. The longer the paper machine is off-line, the worse the situation (high iron content for longer period of time in the condensate). The reason for the iron throw is that the mild steel components went through a contraction and expansion cycle during the shutdown/startup period, causing the oxides to fracture and exfoliate because they are less ductile than mild steel. Additionally, as the system cools down, air is drawn in, and oxygen corrosion attack occurs.

Chemical attack leading to dissolution of the magnetite protective layer will increase the corrosion of mild steel. For instance, high concentrations of caustic or acid can lead to severe corrosion problems in boilers. In addition, chemical species, which interact or complex with the ferrous ion such as chelants, chlorides, sulfates, polymers, and hydroxyl ions, may prevent the formation of magnetite by limiting Eqs. (11.6) and (11.7). The net result of this effect could be an increase in corrosion due to an increase in the rate of metal dissolution.

Polymers and Iron Control

Polymers do play an important role in the iron control strategy; they are the last line of defense. Polymers have the ability to inhibit agglomeration of iron particles, keeping them dispersed in the boiler water, and to reduce the rate of iron oxide deposition on the heat transfer surfaces. The two types of polymers Nalco uses are polymethacrylate and copolymers of acrylate/styrene sulfonate (NexGuard®). These anionic polymers absorb onto the negatively charged iron particles and prevent the particles from agglomerating through charge-charge repulsion and by steric hindrance.

Molecular weight and pH can affect the dispersant properties of anionic polymers. In general, as the pH goes up, the dispersant activity does too. Lower molecular weight anionic polymers are more effective than high molecular weight anionic polymers.

In addition to their dispersant properties, anionic polymers are known to complex iron and solubilize iron in a similar fashion as chelants, although their complexing strength is less than that of chelants. Figure 11.4 illustrates how polymers complex iron.

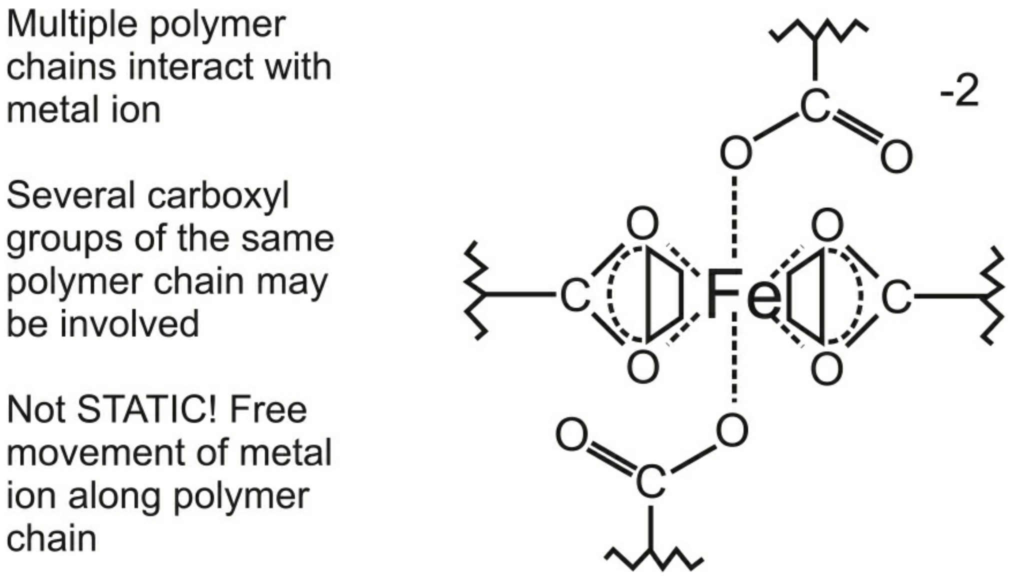


FIGURE 11.4 Polymer complexing iron.

Consequently, polymers can cause feedwater and boiler water corrosion problems. It is important to monitor the generation of soluble iron (Fe^{+2}) and total iron (Fe^{+2} + Fe^{+3}) in the feedwater and blowdown when feeding polymers to determine the optimum product dosage. Total iron testing alone in the feedwater and blowdown cannot differentiate between iron oxide particulate and active corrosion. Figure 11.5 shows the relationship between soluble iron and total iron in boiler blowdown.

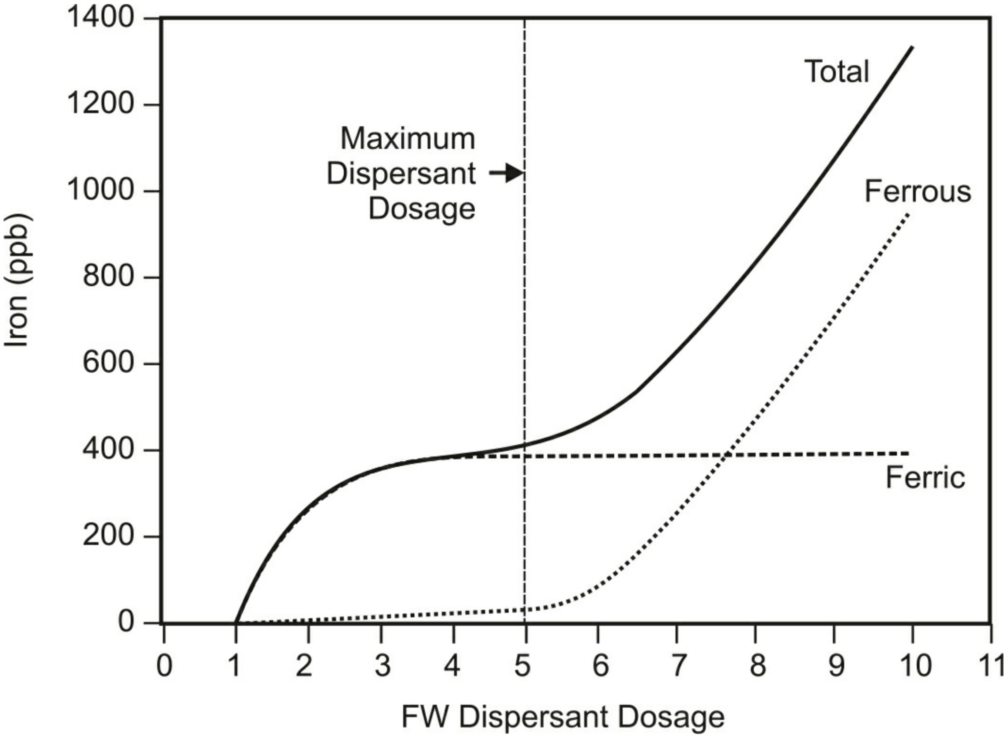


FIGURE 11.5 Soluble versus total iron in boiler blowdown.

As the dosage of the polymer treatment increases, the concentration of particulate iron (Fe^{+3}) increases in the blowdown, then plateaus and remains constant regardless of further increases in dispersant dosage. The initial increase represented the improvement in iron oxide particle dispersion caused by the polymer. As the polymer dosage increases further, ferrous iron (Fe^{+2}) concentration begins to rise in the blowdown, until a near linear relationship between increased dosage and increased Fe^{+2} is established. The data show that increasing the polymer dosage above a certain level does not increase the dispersion of iron oxide particles and their removal, but only leads to increased corrosion.

A good rule of thumb is that the boiler water Fe^{+2} concentration should never be greater than the feedwater Fe^{+2} concentration times cycles, and feedwater Fe^{+2} should be low (2–5 µg/L) in a well-protected system.

Molecular weight, flow, temperature, pH, and polymer concentration affect the corrosivity of anionic polymers toward mild steel. Low molecular weight anionic polymers were found to be more corrosive than high molecular weight polymers. Designing an effective and noncorrosive polymeric iron dispersant for boiler applications requires optimizing chemical structure and molecular weight.

Iron Control

Effective iron control can be summed up in three words: prevention, prevention, and prevention. The best control strategy is to prevent iron from entering the boiler, because iron deposits in the boiler can lead to:

- Under-deposit corrosion problems
- Overheating problems resulting in boiler tube failures
- Unscheduled outages that result in lost production and lost profits
- Higher frequency of boiler acid cleanings
- Increase in capital expenditures

However, since the late 1970s, with the introduction of synthetic polymeric dispersants, the term boiler iron control has come to mean feeding polymeric boiler iron dispersants. In general, focus has been lost on prevention, and the single prong approach or philosophy that one can cure the iron problem by feeding polymer to the boiler and transporting the iron through the boiler has been adopted.

Over the past 20 years, we have learned a lot about iron deposition and control in boilers through extensive laboratory research, field trials, collaborative research studies with Argonne National Laboratory, and published literature from the Electric Power Research Institute (EPRI) and others. Iron transport studies conducted in the field and in our laboratory's experimental boilers indicate that the majority of iron entering the boiler remains in the boiler, even when dispersants are used.

A major reason for the poor transport results is that boilers are not designed to remove suspended materials effectively. The boiler continuous blowdown line is designed to remove soluble species efficiently and is not optimized to remove particulate matter. Surface blowdown will remove some particulate, but it is not isokinetically designed to remove two-phase material (liquid and solids). This is why intermittent manual blowdown of the mud drum is practiced. Another reason for poor transport is that much of the iron reaching the steam generating surfaces of the boiler will deposit and will not be available for removal by blowdown.

However, research work has shown that polymers do affect the rate of iron deposition on the heat transfer surfaces of boilers and, thus, are an important aspect of overall boiler iron control. Polymers can slowdown the rate of iron deposition and help keep the heat transfer surfaces cleaner longer.

Although polymers slow the deposition rate, iron oxide deposition rate follows first-order kinetics with respect to iron concentration. In addition, the higher the heat flux, the faster the rate of deposition. These two findings, coupled with the fact that most of the iron is not transported through the boiler, means that the primary method to control iron deposits in boilers is to prevent iron from entering the boiler in the first place. This statement is strongly supported by the cycle chemistry guidelines published by the American Society of Mechanical Engineers (ASME), EPRI, VGB (a German organization of large power station operators), Japanese Boiler Manufacturers, and the British Boiler Standards. These guidelines stress the importance of keeping the feedwater iron concentration very low (µg/L levels).

As a result of this collective knowledge, the preferred iron control strategy today concentrates on the iron control triangle offense of prevention as shown in Fig. 11.6.

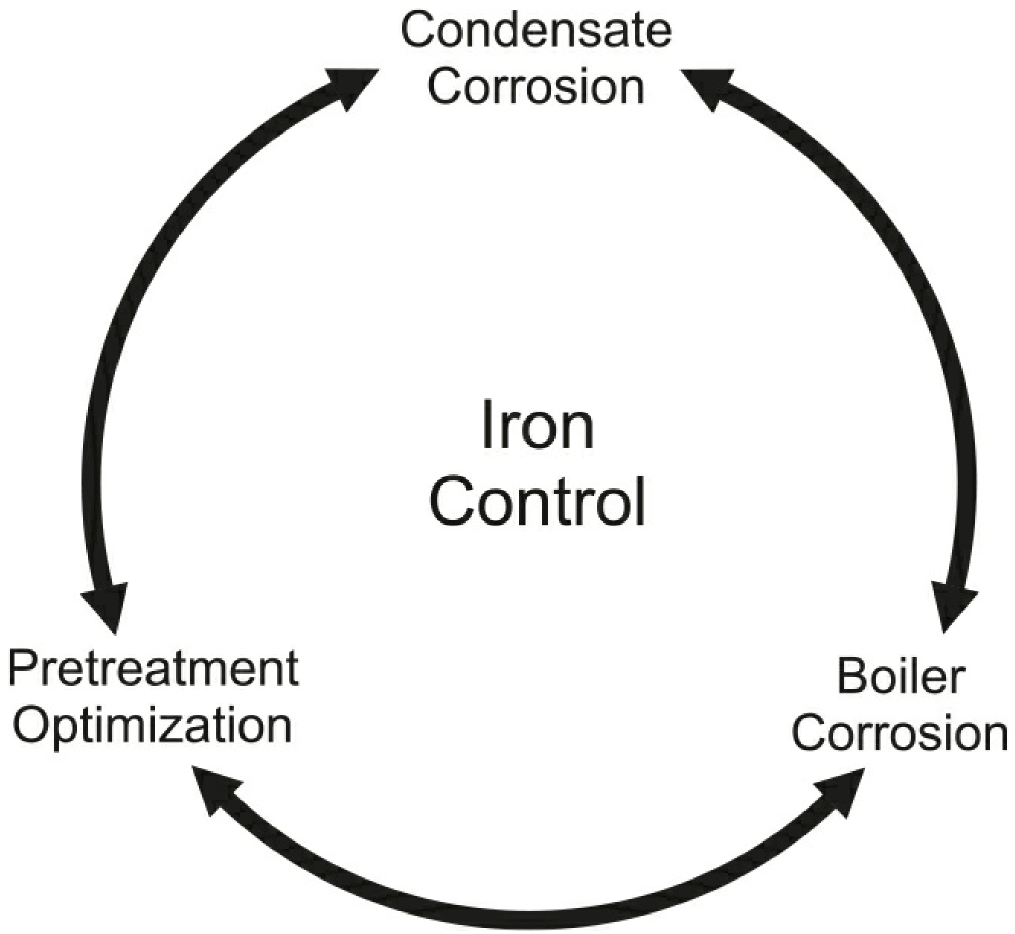


FIGURE 11.6 Iron control triangle.

First, prevent iron contribution from the makeup water by optimizing pretreatment iron removal. Secondly, minimize iron returned via the steam condensate system by inhibiting condensate corrosion and maximizing the removal of any iron present in the returned condensate through use of condensate polishers/filters and automatic dump systems. The third leg of the triangle offense is to minimize corrosion from boiler feedwater and boiler water.

To be successful, the triangle control strategy requires implementing the mechanical, operational, and chemical (MOC) approach, not just a chemical treatment approach. For instance, it is critical to do iron profiling of the makeup water pretreatment system, the condensate system, at the deaerator, at the inlet and outlet of the economizer, and the boiler blowdown. It is necessary to determine where the iron is coming from, how much iron is there, and to determine the form of the iron, in order to identify if the iron is a result of active corrosion (soluble Fe^{+2}) or migration of old iron oxide corrosion products (insoluble particulate Fe^{+3}). Determining the iron removal efficiency and optimizing the performance of plant equipment such as condensate polishers, ion exchange units, carbon or sand filters, and magnetic filters, is very important. Determining if these units are backwashed properly and rinsed down long enough prior to returning the units back into service mode is important because, if done improperly, it may lead to slugs of particulate iron reaching the boiler.

The chemical iron prevention technologies available in the triangle control strategy are:

- Caustic
- Phosphate products
- Organic and inorganic oxygen scavengers
- Condensate neutralizing amines
- Filming amines
- Nonamine filmer (Nalco ACT®)
- Ion exchange resin cleaners (for iron and organic foulant removal)

In the triangle control strategy, iron dispersants are considered defensive chemistries, because they do not prevent iron from entering the boiler.

Preventing iron from entering the boiler is, by far, the best approach to eliminating boiler tube failures caused by iron deposits. Feeding small doses of polymeric iron dispersants (substoichiometric to iron) is warranted, because they can slowdown the iron deposition rate. It is also recommended that boilers not operate at excessively high cycles, because the deposition rate is dependent on the iron concentration. Operating with at least 2% blowdown (50 cycles) in industrial boilers and 1% blowdown (100 cycles) in electric utility boilers is generally effective for good iron control.

Effects of Boiler Scale

Boiler scale creates a problem in boiler operation because all the different types of scale possess a low thermal conductivity. The presence of scale is equivalent to having a thin film of insulation across the path of heat travel from the furnace gases to the boiler water. This heat-insulating material retards heat transfer and can cause a loss in boiler efficiency. Stack gas temperatures may increase as the boiler absorbs less heat from the furnace gases. This is more commonly seen in firetube boilers, where convective heat transfer is more dominant. This is usually not seen in watertube boilers, where radiant heat transfer is the primary mechanism.

The chemical structure of the scale, its porosity, and its thickness, as well as the design and method of operation of the boiler, all influence the amount of heat lost. Heat transfer may be reduced as much as 10 to 12% by the presence of scale. A scale approximately 1/8 inch (3 mm) thick may cause an overall loss in boiler efficiency of 2 to 3% in firetube boilers. In watertube boilers, the presence of scale is more a problem in boiler reliability than efficiency loss.

Even more important than the heat loss is that scale causes overheating of the boiler tube metal and can result in subsequent tube failures. Costly repairs and boiler outages are the results of such a condition. In modern boilers with high heat transfer rates in excess of 150 000 Btu/[h · ft^2] (473 kW/m^2), even extremely thin layers of scale will cause a serious elevation in the temperature of tube metal (Fig. 11.7). The scale coating retards the flow of heat from the furnace gases into the boiler water. This heat resistance results in a rise in metal temperature to the point at which failure can occur.

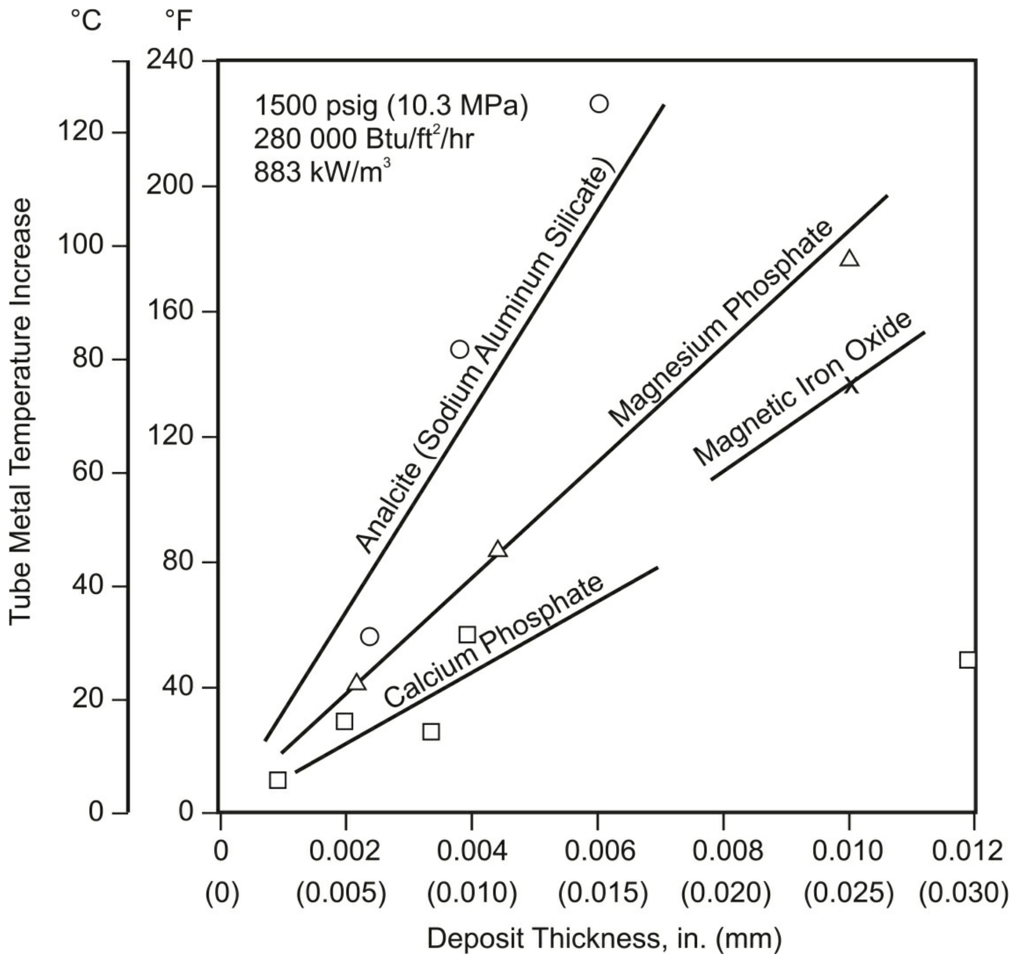


FIGURE 11.7 Effects of boiler scale on tube metal temperature.

Figure 11.8 illustrates the action that takes place in the blistering of a tube because of scale formation. For simplification, temperature drops through gas or water films have not been shown. Section A shows a cross section of the tube metal with a completely scale-free heating surface. There is a temperature drop across the tube metal from the outside metal temperature T_2 to the temperature of the boiler water T_1. Section B illustrates this same tube after a heat-insulating scale layer has formed. In addition to the temperature drop from T_2 to T_1, there would be an additional temperature drop through the scale layer from T_1 to T_0. This condition, of course, would result in a lower boiler water temperature (T_0). However, boiler water temperature is fixed by the operating pressure, and operating conditions require that the same boiler water temperature T_1 be maintained as before the development of the scale layer. Thus, the tube outside metal temperature will be elevated to maintain the same steam generation at the specified temperature and pressure.

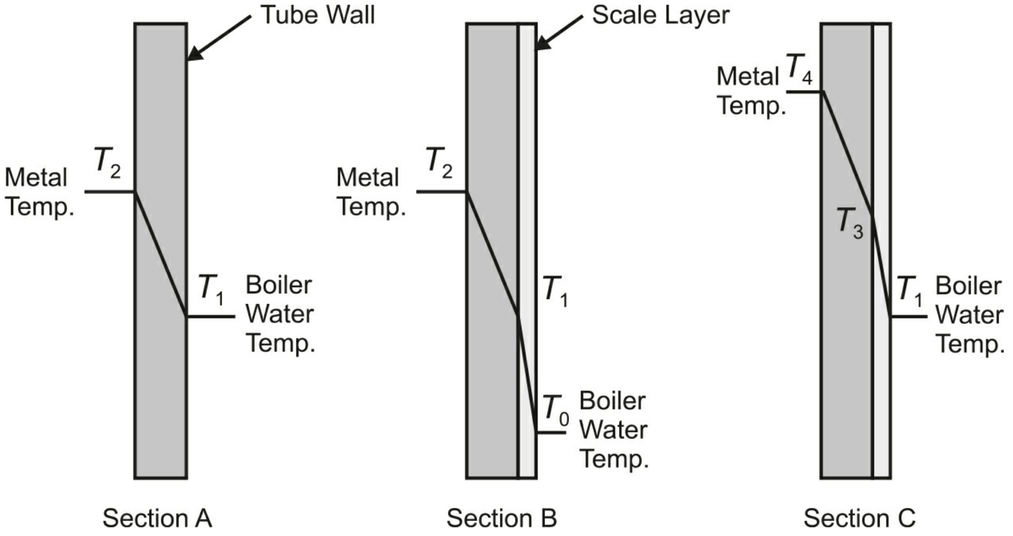
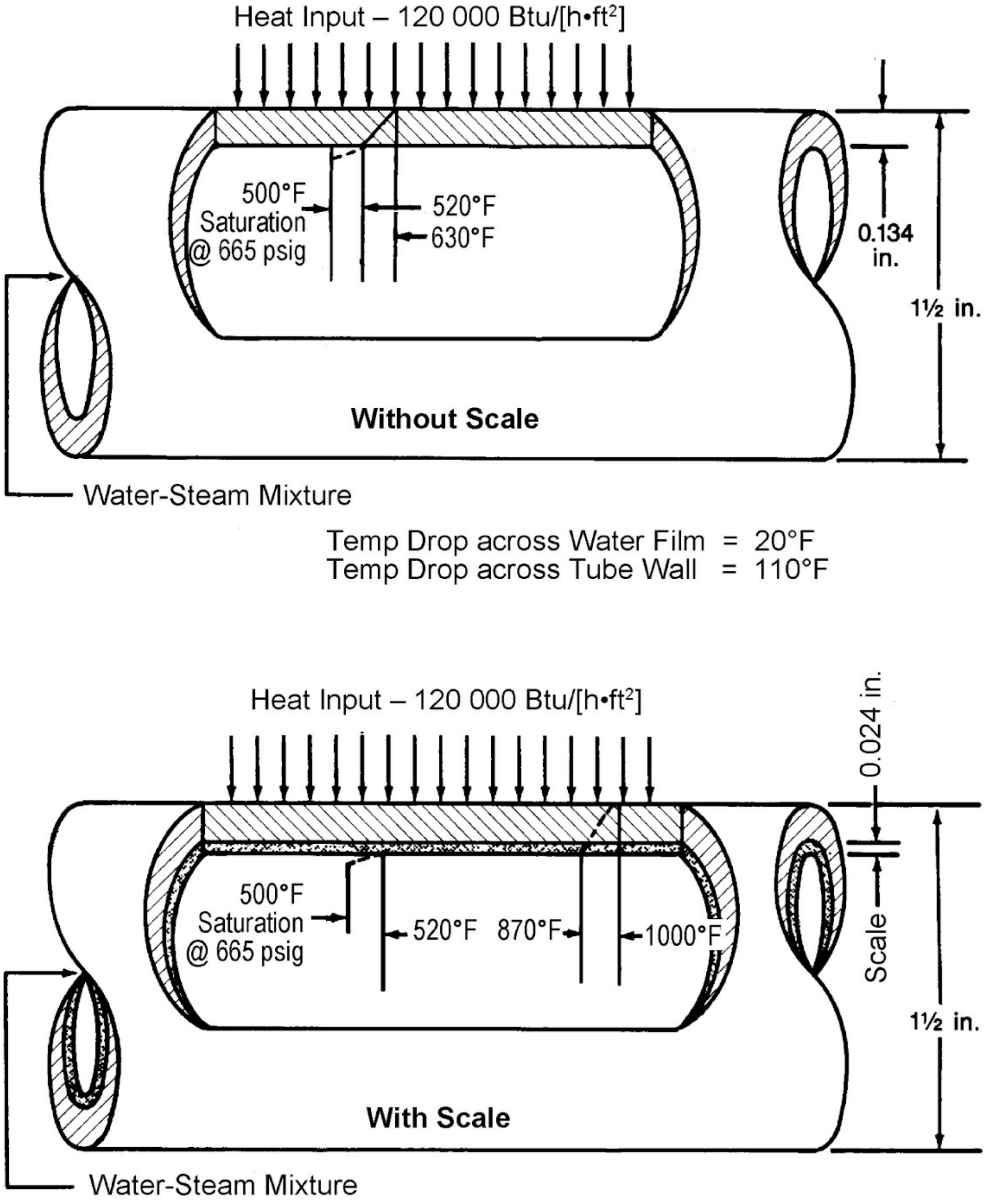


FIGURE 11.8 Effect of scale on boiler heating surfaces.

Section C illustrates the condition that actually develops. Starting at the base boiler water temperature of T_1, the temperature increase through the scale layer is represented by the line from T_1 to T_3. The further temperature increase through the tube wall is represented by the line from T_3 to T_4. The outside metal temperature T_4 is now considerably higher than the temperature T_2, which was the outside metal temperature before the formation of scale on the tube surface.

If scale deposition continues, increasing the thickness of the heat-insulating deposits, tube metal temperature will continue to increase until the safe maximum temperature [usually 900°F (482°C) for the typical carbon steel tube] is exceeded.

Figures 11.9 and 11.10 show the effect of a 0.024 inch (0.61 mm) layer of calcium sulfate scale on a moderately high heat flux boiler tube. The effects of the water/steam film on the inside wall of the tube are shown to further illustrate how only a small amount of scale can quickly result in tube failure. With higher boiler pressures [>1000 psig (6.9 MPag)] and, therefore higher boiler water temperatures, there is less of a temperature difference between the boiler water saturation temperature and the metal. Consequently, in high-pressure systems, even very thin layers of scale can cause failures.



Temp Drop across Water Film = 20°F
Temp Drop across Tube Wall = 110°F

Temp Drop across Water Film = 20°F
Temp Drop across Internal Scale = 350°F
Temp Drop across Tube Wall = 130°F

Assumed $CaSO_4$ Scale (0.024 in. thick)
Thermal Conductivity 0.8 Btu/[h•ft•°F]

Maximum Tube Temp (1000°F) is above Allowable
Oxidation Temp Limit for SA-210 Carbon Steel

FIGURE 11.9 Effect of calcium sulfate scale on high heat flux boiler tube—U.S. units.

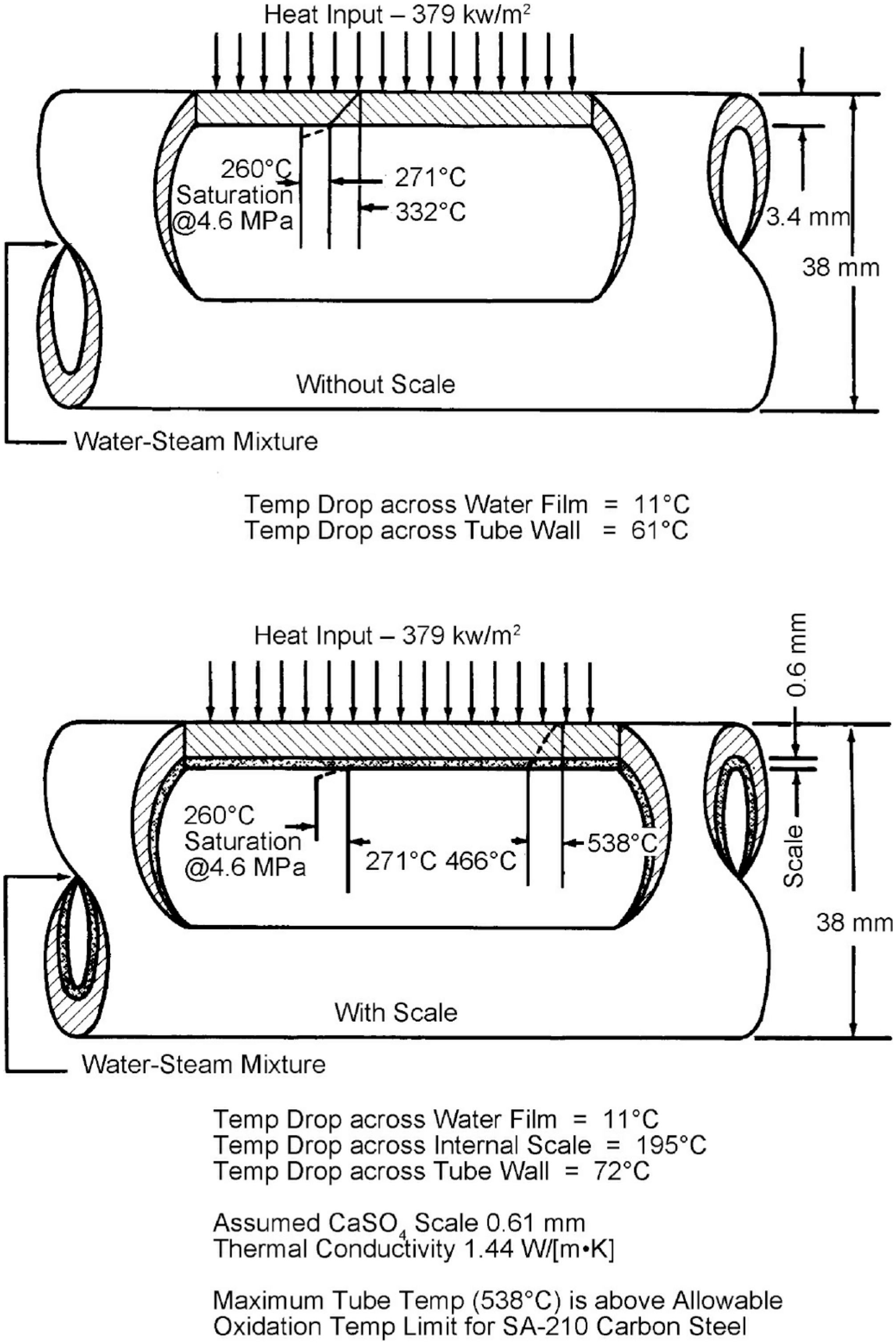


FIGURE 11.10 Effect of calcium sulfate scale on high heat flux boiler tube—metric units.

Additionally, in boilers with high heat transfer rates, scale deposition can promote localized under-deposit corrosion. This secondary corrosion effect is particularly evident in systems that have iron oxide deposition, which are porous deposits. Boiler water can seep through these deposits to the boiler metal, where it will evaporate to steam, leaving behind the dissolved solids. Dissolved solids in the boiler water such as caustic and chloride can concentrate in these localized areas to thousands of milligrams per liter, even though the bulk water contains normal recommended levels of these species. These high concentrations can result in rapid and severe metal dissolution and failure.

Internal Chemical Treatment Programs

Scale formation in low-pressure boilers [<1000 psig (6.9 MPag)] and feedwater systems can be controlled in two primary ways:

1. Proper operation and maintenance of all makeup and feedwater pretreatment systems. Hot and cold lime softeners, filters, sodium softeners, water-cooled packing glands on feedwater pumps, etc., must be operating properly before chemical treatment can be effectively applied. Otherwise, erratic and unpredictable quantities of scale-forming components will be fed to the boiler system, and results will be compromised.
2. Chemical treatment is then used to condition any remaining minerals leaking through to the boiler. Among the treatments in common use today are:
    - Coagulation treatment programs that were commonly used in the past (1900–1950). Although still in use today, modern, inexpensive pretreatment technology has made their use almost obsolete
    - Phosphates (residual with and without polymer)
    - Chelates
    - All-polymer treatments

Phosphate Residual Programs—Low Pressure Industrial Systems

Tricalcium phosphate has an extremely low solubility. Hence, when properly controlled, the addition of phosphate to boiler water removes calcium so completely and efficiently that calcium sulfate, calcium carbonate, and calcium silicate scales can be prevented. In the presence of sufficient alkalinity, the actual phosphate precipitate formed is calcium hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$], which is a less sticky, more readily conditioned reaction product than tricalcium phosphate.

Although phosphate can precipitate with magnesium as magnesium phosphate if the phosphate is overfed, proper boiler chemistry will preferentially precipitate magnesium as a less adherent and more easily conditioned magnesium hydroxide, magnesium silicate, or the preferred lizardite $Mg_3Si_2O_5(OH)_4$ (formerly serpentine). The best solution to boiler scale is proper softening of the makeup water to remove all calcium and magnesium, followed by a good chemical control program.

Phosphate residual programs are acceptable where feedwater hardness is less than 0.3 mg/L.[2] Numerous chemicals can be used to furnish the phosphate ion necessary for internal softening treatment. Compounds of the orthophosphate ion (PO_4^{-3}) are the most widely used. Other phosphate ions that can be used are meta (PO_3^{-}), tripoly ($P_3O_{10}^{-5}$), and pyro ($P_2O_7^{-4}$). Some of these salts are called polyphosphates because they form inorganic polymers. Among these are the glassy sodium polyphosphates (hexa- and heptametaphosphate) and crystalline sodium polyphosphates such as sodium tripolyphosphate and tetrasodium pyrophosphate. The polyphosphates can be described as molecularly dehydrated orthophosphates. When added to water, polyphosphates rehydrate (at a rate that is temperature dependent) to the orthophosphate form from which they were derived.

Although this discussion of phosphates is rather limited, it is a reminder that the precipitation of tricalcium phosphate (or calcium hydroxyapatite) in the boiler can occur only when the phosphate in use has been converted to trisodium orthophosphate by heat and reacted with boiler alkalinity.

If the product is to be fed directly to the steam drum of a boiler, the best choice is an orthophosphate formulation, because the conversion to trisodium orthophosphate (in the case of mono- or disodium orthophosphate) is extremely rapid. Conversely, feeding a meta- or pyrophosphate (polyphosphate) directly to the boiler may delay chemical reactions undesirably. This is particularly true if the boiler pressure is less than 50 psig (345 kPag) and if the cycles of concentration are low (<10). If a phosphate product is fed directly to a boiler steam drum or feedwater, where water temperature exceeds 400°F (204°C), the product should be diluted to less than a 10% solution of the product, or feed the undiluted (neat) product into a feedwater bypass line into the drum. The feed of a concentrated product directly into the steam drum, or feedwater line of greater than 400°F (204°C), may result in plugging the chemical feed line. If, on the other hand, a phosphate is to be fed to the boiler feedwater, a polyphosphate product is chosen to avoid the possibility of deposits caused by softening reactions occurring in the feedwater lines, economizer tubes, etc. An orthophosphate formulation would be entirely unsuitable for such a feed point. When feedwater hardness is greater than 3 mg/L, all phosphates are usually fed to the steam drum to prevent deposition in the feedwater system and the economizer.

Each of the common phosphates has an effect on boiler water alkalinity as well. When hardness in the feedwater is precipitated by direct reaction with alkalinity (as in a coagulation program), available alkalinity generally decreases.

$$\mathrm{Ca(HCO_3)_2 + heat \rightarrow CaCO_3 + H_2O + CO_2} \qquad (11.8)$$

$$\mathrm{CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 + Na_2SO_4} \qquad (11.9)$$

$$\mathrm{Mg(HCO_3)_2 + 4NaOH \rightarrow Mg(OH)_2 + 2Na_2CO_3 + 2H_2O} \qquad (11.10)$$

$$\mathrm{MgCl_2 + 2NaOH \rightarrow Mg(OH)_2 + 2NaCl} \qquad (11.11)$$

When phosphates are used to precipitate the calcium hardness, however, some of the alkalinity associated with calcium hardness is retained in the form of sodium alkalinity in the boiler. The amount of alkalinity retained depends upon the type of phosphate used. Because phosphates must be converted to trisodium orthophosphate in the boiler before precipitation of calcium occurs, some alkalinity consumption results.

$$\underset{\text{(meta)}}{\mathrm{NaPO_3}} + \mathrm{2NaOH} \rightarrow \underset{\text{(trisodium)}}{\mathrm{Na_3PO_4}} + \mathrm{H_2O} \qquad (11.12)$$

$$\underset{\text{(pyro)}}{\mathrm{Na_4P_2O_7}} + \mathrm{2NaOH} \rightarrow \underset{\text{(trisodium)}}{\mathrm{2Na_3PO_4}} + \mathrm{H_2O} \qquad (11.13)$$

$$\mathrm{Na_5P_3O_{10} + 4NaOH \rightarrow 3Na_3PO_4 + 2H_2O} \tag{11.14}$$

(tripoly) (trisodium)

$$\mathrm{Na_2HPO_4 + NaOH \rightarrow Na_3PO_4 + H_2O} \tag{11.15}$$

(disodium) (trisodium)

$$\mathrm{NaH_2PO_4 + 2NaOH \rightarrow Na_3PO_4 + 2H_2O} \tag{11.16}$$

(monosodium) (trisodium)

Once the phosphate has been converted to trisodium orthophosphate, the reactions with calcium hardness proceed, as shown in Eqs. (11.17) and (11.18). Calcium hardness is represented by $CaSO_4$ and $CaCO_3$, although other species may coexist.

$$\mathrm{2Na_3PO_4 + 3CaCO_3 \rightarrow Ca_3(PO_4)_2 + 3Na_2CO_3} \tag{11.17}$$

$$\mathrm{2Na_3PO_4 + 3CaSO_4 \rightarrow Ca_3(PO_4)_2 + 3Na_2SO_4} \tag{11.18}$$

While the overall tendency when using phosphates to soften the water will be to increase the amount of retained alkalinity in the boiler (as compared to coagulation program reactions), the amount of increase is a function of the type of phosphate used. Thus far, only the amount of phosphate consumed in reacting with calcium has been considered. Because a certain level of phosphate residual is always carried (present as trisodium orthophosphate), additional alkalinity is consumed for each mg/L of phosphate residual required [Eqs. (11.12)–(11.16)]. Hence, the net gain in available alkalinity becomes a function of the following:

- Type of phosphate used
- Amount and form of calcium hardness
- Level of magnesium hardness
- Level of residual phosphate carried

These principles can be demonstrated more clearly if the typical calcium-phosphate reactions are considered as one step, rather than as two separate steps. Equations (11.19) to (11.23) demonstrate the effect on retained sodium alkalinity. The reactions controlling magnesium precipitation [Eqs. (11.10) and (11.11)] and those controlling phosphate conversion for phosphate residuals [Eqs. (11.12)–(11.16)] must be added to these reactions.

$$2Na_3PO_4 + 3CaCO_3 \rightarrow Ca_3(PO_4)_2 + 3Na_2CO_3 \tag{11.19}$$

(trisodium)

$$2Na_2HPO_4 + 3CaCO_3 \rightarrow Ca_3(PO_4)_2 + CO_2 + 2Na_2CO_3 + H_2O \tag{11.20}$$

(disodium)

$$2NaH_2PO_4 + 3CaCO_3 \rightarrow Ca_3(PO_4)_2 + Na_2CO_3 + 2CO_2 + 2H_2O \tag{11.21}$$

(monosodium)

$$2Na_5P_3O_{10} + 9CaCO_3 + 2NaOH \rightarrow 3Ca_3(PO_4)_2 + 6Na_2CO_3 + 3CO_2 + H_2O \tag{11.22}$$

(tripoly)

$$2Na_2HPO_4 + 3CaSO_4 + 2NaOH \rightarrow Ca_3(PO_4)_2 + 3Na_2SO_4 + 2H_2O \tag{11.23}$$

(disodium)

Although these reactions are complex, they are important to understanding boiler water chemistry.

Applications

Phosphate residual treatment programs are best suited for feedwaters that are consistently below 0.30 mg/L hardness, have low magnesium, and have silica content greater than one-third the magnesium content. The greater the feedwater hardness is above 0.3 mg/L the greater the deposit accumulation rate will be in the boiler and the greater the need to periodically clean the boiler as well.

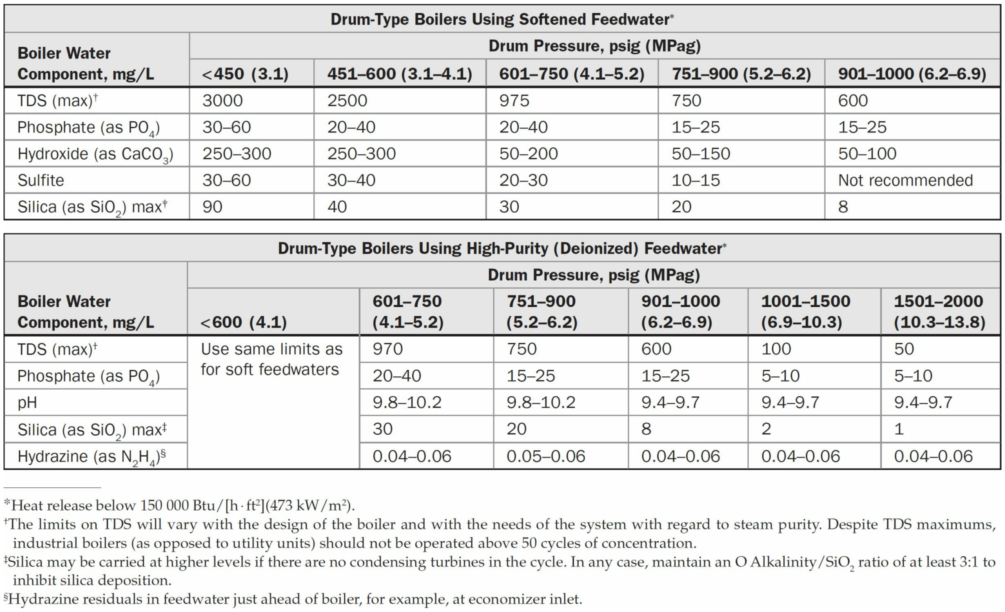
Phosphate programs can be effectively applied to boilers with operating pressures up to 2800 psig (19.3 MPag), although residual phosphate is rarely applied at operating pressures above 1200 psig (8.3 MPag).

Program Controls

Control of a phosphate residual program involves adjusting soluble orthophosphate residuals in the boiler water by adjusting chemical feed rates. It is also important to adjust boiler water hydroxide (O) alkalinity (2P-M); the simple control of P alkalinity alone is not sufficient. As in all programs, proper levels of total dissolved solids, suspended solids, and silica must be maintained.

Phosphate residuals for any given system should be recommended based on boiler operating pressure; however, they should reflect the degree of control capability practical and the consistency of feedwater quality. Hydroxide alkalinity levels are similarly pressure related, and should be set according to individual conditions such as boiler silica levels expected.

Table 11.5 gives optimum limits at various boiler pressures. The values given in this table are guidelines; individual applications dictate the actual acceptable limits.



Drum-Type Boilers Using Softened Feedwater[*]

Boiler Water Component, mg/L	Drum Pressure, psig (MPag) <450 (3.1)	451–600 (3.1–4.1)	601–750 (4.1–5.2)	751–900 (5.2–6.2)	901–1000 (6.2–6.9)
TDS (max)[†]	3000	2500	975	750	600
Phosphate (as PO_4)	30–60	20–40	20–40	15–25	15–25
Hydroxide (as $CaCO_3$)	250–300	250–300	50–200	50–150	50–100
Sulfite	30–60	30–40	20–30	10–15	Not recommended
Silica (as SiO_2) max[†]	90	40	30	20	8

Drum-Type Boilers Using High-Purity (Deionized) Feedwater[*]

Boiler Water Component, mg/L	Drum Pressure, psig (MPag) <600 (4.1)	601–750 (4.1–5.2)	751–900 (5.2–6.2)	901–1000 (6.2–6.9)	1001–1500 (6.9–10.3)	1501–2000 (10.3–13.8)
TDS (max)[†]	Use same limits as for soft feedwaters	970	750	600	100	50
Phosphate (as PO_4)		20–40	15–25	15–25	5–10	5–10
pH		9.8–10.2	9.8–10.2	9.4–9.7	9.4–9.7	9.4–9.7
Silica (as SiO_2) max[‡]		30	20	8	2	1
Hydrazine (as N_2H_4)[§]		0.04–0.06	0.05–0.06	0.04–0.06	0.04–0.06	0.04–0.06

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[*] Heat release below 150 000 Btu/[h·ft²](473 kW/m²).

[†] The limits on TDS will vary with the design of the boiler and with the needs of the system with regard to steam purity. Despite TDS maximums, industrial boilers (as opposed to utility units) should not be operated above 50 cycles of concentration.

[‡] Silica may be carried at higher levels if there are no condensing turbines in the cycle. In any case, maintain an O Alkalinity/SiO_2 ratio of at least 3:1 to inhibit silica deposition.

[§] Hydrazine residuals in feedwater just ahead of boiler, for example, at economizer inlet.

TABLE 11.5 Common Control Limits for Phosphate Residual Programs versus Boiler Pressure

Phosphate-Polymer Programs

Simply stated, phosphate-polymer programs affect the proper calcium and magnesium precipitation reactions, then act to condition the resultant sludge. These programs result in cleaner boilers than are normally seen using a conventional phosphate program.

Phosphate-polymer programs are similar to the phosphate-residual and the phosphate-organic programs in that they use the same precipitation chemistry for calcium and magnesium. There are two important differences between the phosphate-organic and phosphate-polymer programs, however. These are the organic dosage requirements and the boiler water phosphate residual requirements (Table 11.6).

Requirements	Phosphate-Organic Programs	Phosphate-Polymer Programs
Organic dosage	The organic dosage is the amount needed to give a prescribed concentration (equivalent color numbers) in the boiler water and is not based on feedwater harness.	The phosphate dosage is directly proportional to feedwater hardness. Results depend on maintaining this relationship. Boiler water control tests, therefore, are meaningful only when feedwater hardness and boiler water concentration ratios are known.
Boiler water PO_4 residual	PO_4 residual (excess) in the boiler water is maintained simply to insure that all calcium hardness is precipitated as basic calcium phosphate. The boiler water must be tested on a filtered sample.	PO_4 residual provided by phosphate-polymer products serves primarily as an easy means of keeping product dosage at levels needed to maintain correct proportioning of polymer to feedwater hardness. In many cases, this will require higher boiler water PO_4 excess than that needed simply to insure proper calcium precipitation.

TABLE 11.6 Comparison of Phosphate-Organic and Phosphate-Polymer Programs

The organic portion of the phosphate-organic programs, is a blend containing various natural occurring organics. The polymers in the phosphate-polymer product line have a remarkable ability to alter the crystalline structure of the sludge (reaction products), preventing any seeding action and giving exceptional fluidity to the boiler water sludge.

Any use of the word or concept of chelation leads to a quick association with ethylenediaminetetraacetic acid (EDTA) and nitrilotriacetic acid (NTA). There are, however, many chemicals that exhibit chelation properties, including the polymers present in these products. Polymers, however, exhibit a much lower corrosion potential.

Applications

Phosphate-polymer programs are well suited to boilers with feedwater hardness levels up to 0.3 mg/L. (Hardness above 0.3 mg/L can be handled by phosphate-polymer treatment but at poorer economies. Usually, feedwater hardness >0.3 mg/L calls for corrective action.) For ion exchange softened feedwaters, except where iron is the sole or primary contaminant, phosphate-polymer programs normally give better results than conventional phosphate-organic programs.

The phosphate-polymer programs have the same advantages and disadvantages as the conventional phosphate programs, with two exceptions:

1. Phosphate-polymer programs can provide much cleaner boilers than the conventional phosphate programs.
2. Much stricter control is required with these programs. Chemical dosages must be adjusted corresponding to feedwater hardness fluctuations to maintain the proper phosphate-to-hardness ratio.

Program Controls

Phosphate-polymer programs are controlled by phosphate residual readings on a filtered sample of the boiler water blowdown. In most cases, the phosphate control range will be established by normal product dosage calculations.

Special Considerations

At normal use dosages, the deposit removal capability of the phosphate-polymer products is dramatic. Deposit removal occurs by sloughing, which can block tubes and headers.

If, after inspecting a boiler, acid cleaning seems warranted, then the boiler should be cleaned. Do not try to substitute a phosphate-polymer treatment for an out-of-service cleaning. The odds are very much against such an approach succeeding. Online boiler cleaning is never recommended.

When a phosphate-polymer program is recommended for any boiler, except a new or a freshly cleaned one, special precautions should be taken. Where possible, schedule an inspection in 60 to 90 days to observe the condition of the boiler, particularly the lower areas, such as water-wall headers, near-horizontal tube runs, and the mud drum at the blowdown connection. Remove any accumulations of chip scale or sludge before putting the boiler back in service. During the first few months of operation on a phosphate-polymer program, increase the frequency of bottom blows, where applicable, to facilitate removal of materials sloughed from boiler surfaces. This should be done with greater frequency when turbidity levels increase in the boiler water.

If a phosphate-polymer program does not appear to be producing good results in an oil-contaminated system, change to a phosphate-starch organic product. The starch organic should help in handling the oil. The source of the oil contamination should be located and eliminated.

Very little, if any, change has been noted in the composition of sludge formed on a phosphate-polymer program as compared with sludge formed on a standard phosphate-organic program. Normal calcium and magnesium reaction products are formed, and normal interpretation of results can be made. There are visible differences, though. In the absence of dark lignin organics, the sludge is very light buff in color. The light film formed on metal surfaces may also appear grainy or granular. Light finger pressure will usually remove the light film, exposing the boiler metal. The volume of sludge will be proportional to the feedwater hardness levels.

Phosphate Programs—High Pressure Industrial Systems

Sodium phosphates provide the desired pH in boiler water, while controlling the presence of free sodium hydroxide, as shown by these hydrolysis reactions:

$$\mathrm{Na_3PO_4} \rightleftharpoons \mathrm{3Na^+} + \mathrm{PO_4^{-3}} \qquad (11.24)$$

(trisodium phosphate)

$$\mathrm{Na_3PO_4} + \mathrm{H_2O} \rightleftharpoons \mathrm{Na_2HPO_4} + \mathrm{NaOH} \qquad (11.25)$$

$$Na_2HPO_4 \rightleftharpoons 2Na^+ + HPO_4^{-2} \tag{11.26}$$

(disodium phosphate)

$$HPO_4^{-2} \rightleftharpoons H^+ + PO_4^{-3} \tag{11.27}$$

$$Na_2HPO_4 + H_2O \rightleftharpoons NaH_2PO_4 + NaOH \tag{11.28}$$

$$NaH_2PO_4 \rightleftharpoons Na^+ + H_2PO_4^- \tag{11.29}$$

(monosodium phosphate)

$$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{-2} \tag{11.30}$$

The practice of "congruent phosphate" treatment relies on the use of disodium and trisodium salts of phosphoric acid. The practice of "equilibrium phosphate" or "phosphate continuum" treatments relies on the use of trisodium phosphate with up to 1.0 mg/L of caustic soda (NaOH). Where the sodium (Na) to phosphate (PO_4) molar ratio in pure water is 3:1.

Controlling pH solely by sodium phosphate hydrolysis, bulk boiler water pH should never accidentally increase to levels aggressive to boiler steel. Equation (11.25) shows that the hydrolysis reaction of trisodium phosphate is self-limiting as this reaction does not proceed to dryness. As pH rises above 10, generation of hydroxide ions by hydrolysis decreases. It is theoretically impossible for a solution to reach a pH much above 12. If the Na_3PO_4 solution were to concentrate to 10 g/L, the pH would be 12.

Sodium hydroxide generated solely by this hydrolysis reaction is sometimes called "captive"; it will be "taken back" and revert to Na_3PO_4 at any sites of localized evaporative concentration. In theory, high concentration of NaOH in a confined area where solids might form is avoided, preventing caustic gouging of the metal. Thus, it was believed that maintaining a less than 3:1 Na/P molar ratio (coordinated phosphate control) in the boiler water would provide positive protection against the caustic concentration type of corrosion damage.

In Eq. (11.25), if water were to be removed by evaporation, the equilibrium would be forced to the left. In theory, upon evaporation to complete dryness, the residue would contain Na_3PO_4 free of NaOH. However, in the actual case of complete evaporation, even though Eq. (11.25) doesn't predict NaOH, due to the incongruent precipitation behavior of sodium phosphates, NaOH is formed and caustic stress corrosion cracking (SCC) is a potential issue at this highly stressed location. If these connections leak in service, then caustic SCC damage of the drum could occur, if the boiler water were allowed to contain free caustic.

Congruent phosphate chemistry control [sodium-to-phosphate molar ratio ($Na:PO_4$) less than 2.6:1, the "congruent ratio"] is required to prevent the formation of free hydroxide (OH^-) in this situation. This Na/P congruent ratio is temperature dependent and varies from 2.85:1 at lower pressures to 2.6:1 at higher pressures. Congruent phosphate control would still be the preferred phosphate chemistry to use in most industrial boilers that have mechanical tube-to-drum connections and the requisite feedwater purity unless they were having phosphate hideout issues.

In the past, in order to minimize the potential for caustic corrosion, treatment programs focused on maintaining the $Na:PO_4$ molar ratio less than 3. Control schemes varied. Plants employed congruent and coordinated phosphate treatments at various times. All of these phosphate treatment programs sought to restrict the boiler water sodium-to-phosphate molar ratio to less than three. These treatment programs were predicated on the belief that caustic corrosion posed a greater risk than acid corrosion. As boiler operating pressures increased, the susceptibility of these boilers to phosphate hideout especially on congruent control became greater, and the potential for phosphate wastage damage increased.

More recent data suggest that phosphate corrosion represents a significant risk too. The presence of up to 1 mg/L of free caustic ($Na:PO_4$ molar ratio >3) in the bulk water minimizes the possibility of phosphate hideout. These higher operating pressure boilers utilize all-welded construction (no tube-to-drum mechanical connections) and therefore, do not have to be concerned about susceptibility to SCC with this low level of free caustic in the boiler water.

EPRI updated its phosphate treatment recommendations in 1994 to create the Equilibrium Phosphate Treatment (EPT) and Phosphate Treatment (PT) programs. Congruent phosphate treatment was dropped from the guidelines in 1994, although it continued to be practiced in the utility industry. The EPT and PT programs limited the sodium-to-phosphate molar ratio to 3.0 + 1 mg/L

NaOH (on the high end) and 2.8 (on the low end). At higher phosphate concentrations, the program was called phosphate treatment and at lower phosphate concentrations, it was called equilibrium phosphate treatment (Fig. 11.11.) The dividing line was the "equilibrium" phosphate level and plant specific. In practice, few plants determined their equilibrium phosphate level and instead relied on a hybrid treatment somewhere between EPT and PT.

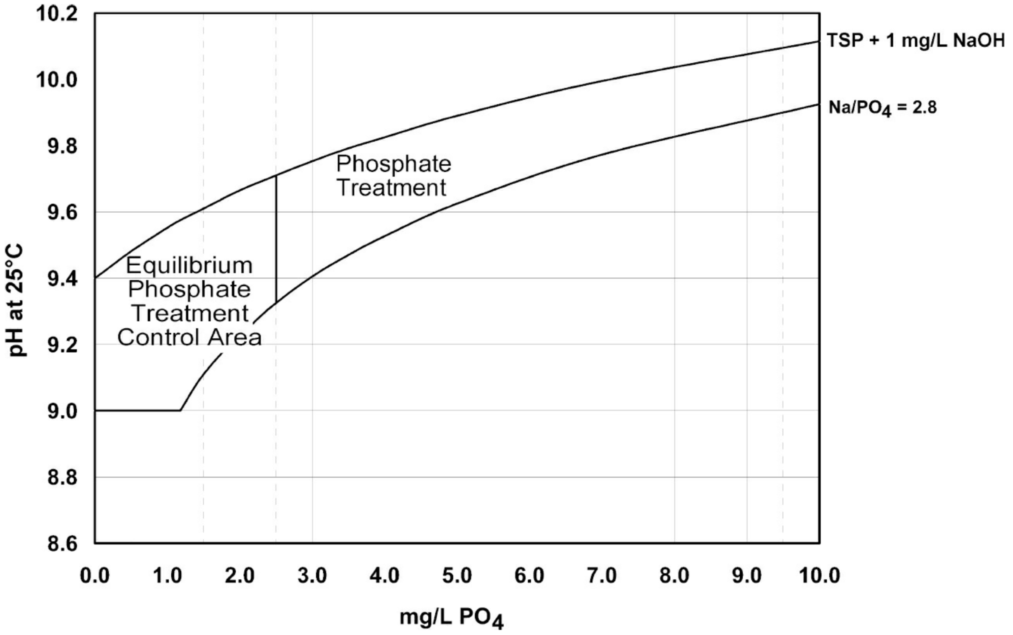

FIGURE 11.11 Traditional PT/EPT control chart.

The PT program is not similar to the coordinated phosphate program of the past. The EPT program was designed for units experiencing phosphate hideout, but that could not use all-volatile treatment (AVT) or oxygenated treatment (OT), due to the potential for feedwater contamination. The EPT program was essentially a low-level phosphate treatment (PT) program, with hideout setting plant specific limits for phosphate and hydroxide.

In retrospect, the EPT program provided too little pH buffering at very low (< 0.2 mg/L) phosphate concentrations. In addition, incorrect implementation of the limits at the plant level, resulted in several cases of subsequent hydrogen damage.

While an improvement over previous boiler pH control programs, EPRI sought to minimize the problems with the EPT/PT program and in 2004 issued its new recommendations, phosphate continuum (PC).

The continuum control strategies increase the minimum Na:PO$_4$ ratio to 3.0

with a maximum bounded by the trisodium phosphate (TSP) + 1 mg/L NaOH line. The minimum boiler water pH is 9.0 regardless of program type. The minimum phosphate is 0.2 mg/L. Plants attempting to control phosphate below this value are essentially using all-volatile treatment, and need to have feedwater purity to support AVT. Figure 11.12 illustrates the new limits.

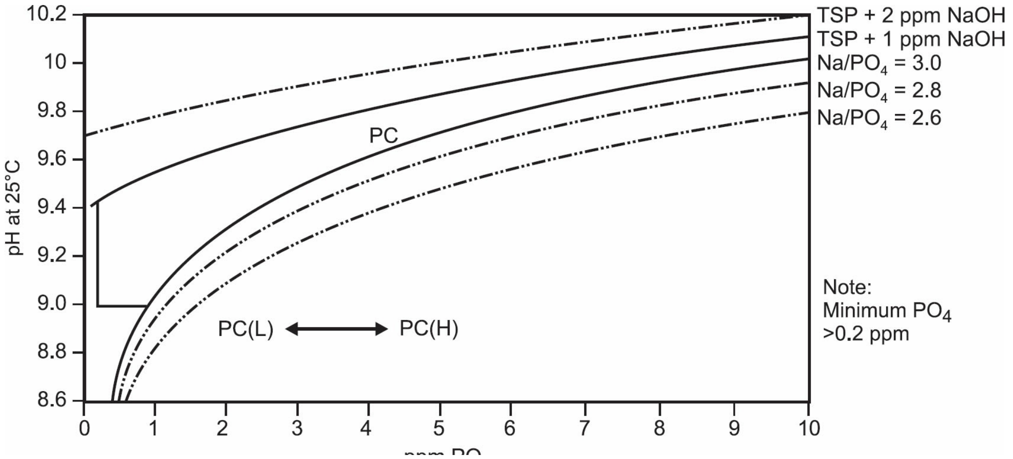

FIGURE 11.12 Phosphate Continuum control chart for high-pressure boilers.

The continuum control strategy eliminates the former dividing line between EPT and PT. Instead, the continuum program continues to transition as phosphate increases greater than 3 mg/L. Both areas are now combined to form the “phosphate continuum” (EPRI terminology). This new strategy requires tighter pH control, and product selection becomes critical. In general, only products with Na:PO_4 ratio greater than 3.0 are used. Disodium and monosodium phosphates are no longer typically used. In the electric utility industry note that the continuum treatment assumes feedwater can consistently meet the required purity guidelines. Plants with a source of sodium contamination, most often from the use of a two-bed demineralizer more common in the industrial steam generation systems, may have to feed disodium phosphate to obtain the desired Na:PO_4 ratio in the boiler water.

This new PC approach provides several benefits. It provides better pH control and buffering, greater tolerance of low-level feedwater contamination, reduced potential for phosphate attack (if hideout occurs), and easier control.

Chelates and Chelate-Polymer Programs

The nature of metal ions and how they behave must first be understood before discussing chelation and the use of chelating agents in the control of metal ions. When metal-containing compounds are ionized in water, the metallic component exists as a positively charged, freely moving ion in the solution. These free metal ions react to surround themselves with negative ions or polar molecules that are present in the solution. The number of such molecules or negative ions that coordinate with the metal ion varies, but for most metals it is usually four or six. These centers of activity of the metal ion may be termed reactive sites. In general, the reactions caused by free metal ions in solution are due to these reactive sites.

In an aqueous solution containing only a simple metal salt, the reactive sites will be occupied by water molecules. When materials are added that interact more strongly or compete more effectively than the water molecule for the reaction site, the sheath of water molecules is displaced, and the metal ion acquires new properties. An example of this is the reaction of copper ions with ammonia (Fig. 11.13).

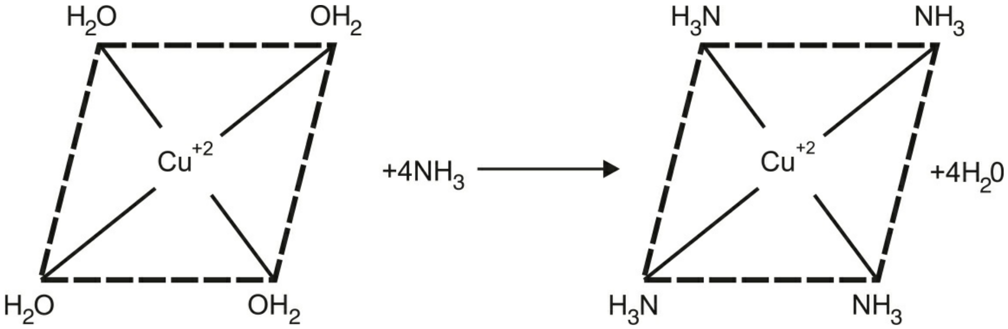

FIGURE 11.13 Copper ions with ammonia.

The water molecules being held at the four reactive sites of the copper ion are displaced by ammonia. The ammonia forms a stronger attachment to the copper ion than does the water, so the resultant ammonia-copper complex is more stable. The ammonia can be displaced by adding some material capable of forming a still more stable complex with copper.

The common metal-complexing agents form complexes in which one molecule of the complexing agent coordinates with one reactive site of the metal ion. Thus, in Fig. 11.13, one ammonia molecule fills one reactive site of the copper ion. However, when the ammonia is replaced by ethylenediamine (a molecule made up of two amine groups connected by an ethylene bridge), a different type of compound results. The two complexing groups in the ethylenediamine molecule incorporate the copper or other metal ion, such as calcium or magnesium, into a ring-type structure (Fig. 11.14). The metal ion is said to be chelated, and ethylenediamine is termed a chelating agent. Thus, chelation may be defined as an equilibrium reaction between a metal ion and a complexing agent, characterized by the formation of more than one bond between the metal and a molecule of the complexing agent and resulting in the formation of a ring structure incorporating the metal ion.

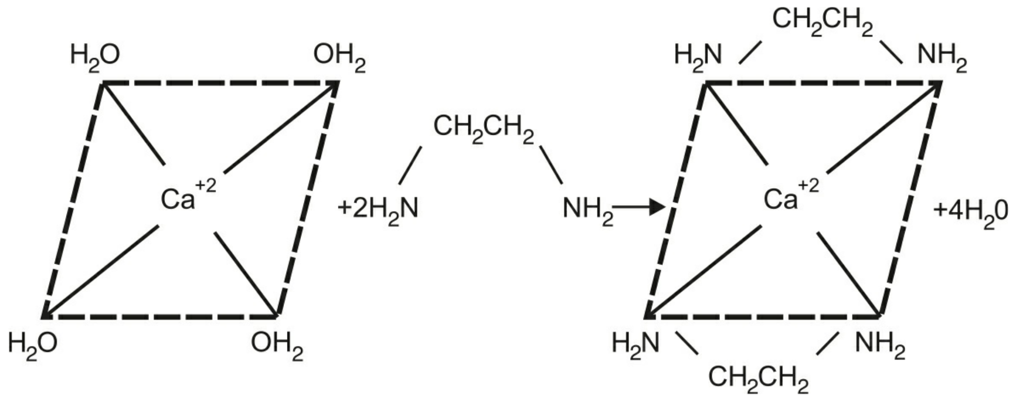

FIGURE 11.14 Calcium ions with ethylenediamine.

Chelating agents control metal ions by blocking the reactive sites of the metal ion and preventing it from entering into its normal (and in many cases undesirable) reactions.

Metals chelated by chelating agents are still present in the system. They are inactivated because their reactive sites are blocked and, therefore, they can no longer undergo reaction or cause reactions in the system. This change in the nature of the metal ions is reflected by changes in their physical properties, which decreases the availability of the metals to react with other anions.

The word chelate derives from the Greek chele, meaning claw. The word chelate was probably chosen because of the structure of the molecule, which holds the metal that has been chelated tightly in a ring structure. The resulting complex is quite soluble and will not permit the hardness metals, calcium and magnesium, to deposit in the boiler as carbonates or sulfates. Although this complex is quite stable under boiler conditions, strong competing anions such as phosphate, silicate, and hydroxide can form insoluble precipitates with the hardness ions in the presence of chelates. Since this type of reaction is an equilibrium between the metal ion and the chelate, a slight excess (residual) of the chelate is required to maintain the metal ion in solution. If the residual chelate is excessive, however, corrosion of the boiler metal may result.

In boiler applications, the two most common chelates used are ethylenediaminetetraacetic acid (EDTA) and nitrilotriacetic acid (NTA).

Applications

Chelating agents must be fed continuously into deaerated feedwater. Chelating agents do not react successfully under oxidizing conditions, because either the chelating agent or the resulting complex breaks down. The presence of any oxygen significantly increases the potential for corrosion by the chelating agent; therefore, an oxygen scavenger must be fed ahead of the feed point of the chelating agent.

Concentrations of chelate residuals, both NTA and EDTA, should never exceed 20 mg/L (as $CaCO_3$) in the boiler water, because corrosion is a definite possibility if this range is exceeded. Control for all products is by measurement of residual (unreacted chelate expressed as $CaCO_3$). Suggested control ranges are shown in Table 11.7 as a function of boiler pressure. Where the possibility of concentration mechanisms or film boiling exists in a new or existing boiler, chelates should not be used, unless a hydrogen corrosion study has been done to determine their effect on the boiler.

Boiler Pressure, psig (MPag)	Chelate Residual, mg/L as $CaCO_3$
400 (2.8)	4–8
401–600 (2.8–4.1)	3–6

TABLE 11.7 Suggested Control Ranges for Chelate Residuals

Special Considerations

Alkalinity requirements of the boiler water are the same as those for a conventional phosphate-organic treatment program. The lowest practical O alkalinity is 120 mg/L. O alkalinity is important and must be determined by the barium chloride titration method. P alkalinity alone is not a sufficient control parameter, because it includes one-half of the carbonate alkalinity as well as the hydrate alkalinity.

Silica control is the same whether a chelating agent or a phosphate-polymer is used. Because the major purpose of silica control is to reduce steam contamination (and turbine fouling), boiler pressure is the criterion for determining the maximum silica limit. Operating experience does not indicate any noticeable positive benefits of chelating agents on silica.

Cycles of concentration should be controlled to minimize the breakdown of chelated complexes at the heat transfer surfaces. Chelates are organic molecules and are therefore subject to thermal degradation. Although the chelated metal ions are somewhat thermally stable, breakdown of the complexes can occur, with the EDTA complexes being less stable than the NTA complexes. When thermal breakdown of the complex occurs, the metal ion is released and will precipitate on the heat transfer surfaces as scale. Thermal breakdown is a function of temperature and time. If the residence time in the boiler is minimized, the formation of scale will also be minimized. The residence time in the boiler can be minimized by controlling the concentration to 50 cycles or less. Additionally, the residual chelate is more subject to thermal degradation than is the chelated complex. This degradation is dependent on temperature, time, and oxygen. This is particularly true of the EDTA molecule. The initial breakdown products of EDTA are weak chelates but are not detected in the test for residual chelate. These breakdown products can be corrosive to the boiler metal.

In some cases, chelate products are formulated with polymers. This combination can be very corrosive to boiler metal, particularly when the boiler makeup water is demineralized where there is no hardness for the chelate to complex. The corrosion from the combination of chelate and polymer can be more severe than either chelate or polymer alone.

Dissolved solids should be maintained at the same level as with a conventional phosphate-organic treatment program. Products containing antifoam will provide additional protection, but total dissolved solids must still be controlled as with a conventional program.

Continuous feed of any chelating agent to the feedwater is necessary. Accurate control is essential, so a chemical pump and solution or day tank are required. Chelating agents are corrosive to mild steel at high concentrations (above 5%) and temperature greater than 100°F (38°C). Therefore, chelate solutions should be fed from either stainless steel or polyethylene feeding equipment.

Application of chelates should be to the feedwater line only. A quill injector, stainless steel piping, and shut-off valve must be used at the point of entry into the feedwater line. The feedwater at the point of chelate injection must be completely deaerated and should carry a residual oxygen scavenger.

Online cleanup of an operating boiler should not be recommended, because sloughing deposits can cause blocked tubes and subsequent tube failures. A dirty boiler should be acid cleaned off-line by a qualified cleaning company.

Applied product dosages should be no greater than the theoretical dosage required to complex all feedwater hardness and to supply desired chelate residual in the boiler. If the chelate residual does not appear in the boiler at this theoretical dosage, do not increase chemical feed rate, unless the variables for the dosage calculation have changed (i.e., feedwater hardness has increased or boiler concentrations have decreased). The residual will appear in time as long as the theoretical dosage is maintained. Increasing chemical feed in lieu of changes in theoretical demand will cause more rapid sloughing of deposits from surfaces, which may result in circulation restrictions and subsequent tube failures.

All-Polymer Programs

Nalco was the first company to introduce all-polymer boiler internal treatment programs to the market (1980). Designing an effective all-polymer boiler treatment is very complex. There are a number of critical chemical and physical properties that must be considered and evaluated when developing an all-polymer program:

- The polymer structure and its molecular weight profile
- Hardness complexing ability
- Stability under boiler operating conditions
- Dispersant capacity
- Oxygen stability
- Solubility of the polymer-hardness complex
- Breakdown mechanism, products, and temperature
- Toxicity of breakdown products and effects on boiler
- Corrosiveness of polymer
- Regulatory status

All-polymer programs contain no chelants, phosphates, or phosphonates and require no supplemental dispersant to be effective. They function by dispersing particles such as iron oxides and boiler sludge and by complexing individual hardness ions to prevent the precipitation of mineral scales.

The polymers used for boiler treatment are formed from monomers having carboxylic acid functional groups and are called polycarboxylates. Acrylic acid and methacrylic acid are the carboxylate monomers that Nalco uses in its boiler polymers. Some polymers also contain styrene sulfonate monomer. The polycarboxylates are anionic in the alkaline pH range.

Polycarboxylates have an attraction toward the surfaces of particles in the boiler water and can adsorb on those surfaces. The particles can be iron oxides or mineral scales and boiler sludge that precipitate from solution inside the boiler. When the polymers adsorb on the surfaces of particles, they enhance the surface electrical charge and increase the repulsive force between the particles. The large polymer molecules also form a physical coating on the particles that reduces the possibility of agglomeration or deposition on the heat transfer surfaces. This mechanism is called dispersion, and the polymers can be called dispersants or sludge conditioners. Polymers are uniquely effective dispersants, but small molecules such as chelants do not function in this manner.

All-polymer programs inhibit hardness scale formation by maintaining the solubility of calcium and magnesium ions. The solubilization mechanism involves complexation of hardness by the carboxylate functionality of the polymer. The reaction can be simply illustrated as shown in Fig. 11.15.

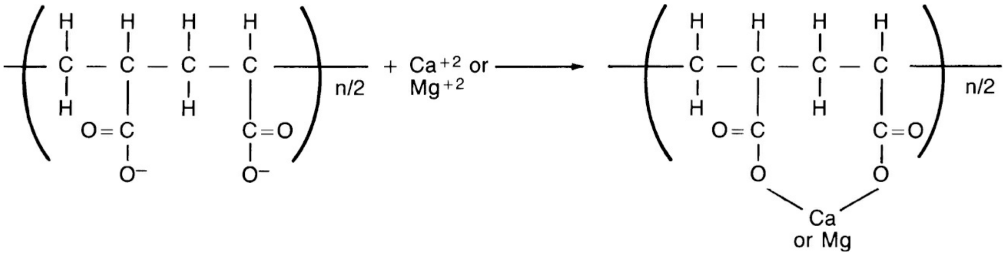

FIGURE 11.15 Polymer solubilization mechanism.

The carboxylates form strong bonds with the hardness ions. Since the polymers have many possible binding sites and are flexible molecules, the binding is maintained even at high temperature. While this binding is excellent for inhibiting the formation of hardness scale under normal conditions, it does have a drawback. During hardness excursions (e.g., softener breakthrough or condensate contamination), some types of polymers can be overwhelmed by excessive calcium concentration, and a neutral calcium polyacrylate complex can precipitate from solution. This calcium polyacrylate precipitate can form adherent deposits on the boiler heat transfer surfaces. This precipitation process removes the polymer from solution, and mineral scales such as magnesium silicate can form rapidly during calcium polyacrylate deposition episodes.

A copolymer of acrylic acid and styrene sulfonate was developed to avoid the calcium polyacrylate problem. The sulfonate group does not bind hardness and maintains a negative charge on the polymer even in the presence of high concentrations of calcium. The negative charge keeps the polymer soluble so it does not become incorporated in the scale. The soluble polymer maintains its dispersant activity and inhibits the deposition of hardness scales that may be precipitating during the upset condition.

Applications

Although far less aggressive than chelants (EDTA and NTA), polymers can bind individual iron ions and participate in corrosion reactions. These reactions are greatly accelerated by high flow rate or turbulence. Care must be taken to dose polymers properly, especially in systems with very low hardness or demineralized feedwater. Feed point location is also important, and injection of neat polymer products directly in front of turbulent areas such as pumps or elbows should be avoided. Corrosion caused by chelants or polymers can be detected and gauged by the use of the Fe^{+2} test.

Polymer dosage should be based on a statistical upper control limit, not merely on average total feedwater hardness. Severe hardness upsets or underdosing of acrylate/acrylamide polymers (20% of recommended) may result in the formation of calcium polyacrylate deposits. If a major upset (outside the control limit) occurs, product feed must be increased to recommended levels, and blowdown must be increased accordingly. Copolymers of acrylic acid and styrene sulfonate will not form calcium polyacrylate, but both dosage and blowdown should be increased during hardness upsets.

Fifty cycles of concentration should be considered the maximum for industrial boilers. Over cycling does not allow for proper purging of boiler water solids, which can be extremely high during upset conditions. All-polymer programs are organic in nature and therefore susceptible to thermal degradation, which is a function of temperature and time. Operating at high cycles can cause thermal degradation of polymers and poor performance. This is particularly true for iron deposit formation. If operation above 50 cycles is required, the boilers will require high-purity feedwater (demineralized) and condensate polishing or filtration to remove iron particulates. Only high stability polymers should be used. The ASME guidelines for boiler water quality (Consensus on Operating Practices for the Control of Feedwater and Boiler Water Chemistry in Modern Industrial Boilers, latest edition) should be followed.

Program Controls

Polymer programs should be controlled by testing for the active polymer, or by a combination of testing for traced fluorescence technology (TRASAR® technology) and active polymer. Traced fluorescence technology is a nonvolatile, nonprecipitating, and nonreactive chemical that can be fed into the boiler feedwater. The concentration of traced material can be measured by the fluorescence of a water sample. The ratio of the concentration of traced material in the boiler water divided by the traced material concentration in the feedwater is the cycles of feedwater concentration in the boiler water. Traced fluorescence technology testing can be used as a routine method for grab sample analysis or online control.

When using traced fluorescence technology as a routine control method, the active polymer concentration in the boiler water should be tested to confirm good polymer recovery. The organic polymers can be subject to some thermal degradation, especially in boilers operating above 600 psig (4.1 MPag). Oxygen ingress can cause polymer degradation in any boiler system. Occasional polymer recovery testing will detect any problems with thermal or oxygen degradation and prevent performance problems.

Polymer recovery testing is accomplished by measuring product concentration by traced fluorescence technology and comparing that value to product concentration measured by active polymer testing. In boilers operating normally, the boiler water product concentration by active polymer testing should be 80 to 100% of the traced fluorescence technology product concentration.

Advantages and Disadvantages

All-polymer programs offer several advantages over other scale control programs, such as:

- Produce the cleanest heat transfer surfaces and highest boiler efficiency
- Transport 100% of hardness through the boiler
- Excellent iron and sludge dispersion to maintain cleaner heat transfer surfaces
- Can be applied to virtually any type of boiler, including waste heat boilers
- Copolymers of acrylic acid and styrene sulfonate do not form calcium acrylate deposits when underdosed because of feedwater hardness upset conditions
- The program is nonvolatile, so it is safe for turbine operation
- Program control tests are easy
- The polymers do not interfere with hardness testing
- FDA/CFIA (Canadian Food Inspection Agency) approved
- Traced fluorescence technology compatible

Disadvantages include:

- Limited to boilers operating at pressures below 1000 psig (6.9 MPag)
- Feedwater hardness limits of 0.02 to 3.0 mg/L as $CaCO_3$
- Can be corrosive if overfed
- Can release chip scale (do not feed to dirty boilers)

Special Considerations

Any polymers containing acrylamide will contribute significant concentrations of ammonia to the steam from the thermal hydrolysis of the amide. Nalco has moved away from using such polymers for boilers. High ammonia concentrations can result in an artificially high pH in the final condensate. If, when using an acrylamide-containing polymer, condensate treatment is decreased and the condensate pH remains high, it is imperative to check condensate iron values and to check system pH at intermediate locations, not just at the bulk condensate return.

Ammonia release from acrylamide-containing polymers can be corrosive to any copper alloys present in the feedwater and condensate system. Generally, 300 to 500 µg/L of ammonia can be tolerated in a copper alloy-containing feedwater system, depending upon dissolved oxygen content. If higher oxygen concentrations are present, lower concentrations of ammonia are required to reduce copper corrosion.

All-polymer products contribute sodium to steam generation systems; therefore, extreme care should be used when applying these products to higher-pressure systems as an overlay to coordinated phosphate or congruent phosphate programs.

If the boiler is operated properly and no carryover exists, then polymers present no steam contamination issues. However, in certain types of systems (refineries, ammonia plants, etc.), economic risks are present in the form of poisoned catalyst if boiler water is carried over into the steam. In systems containing turbines, boiler water carryover can damage or impair turbines. To prevent problems in the areas of steam use, it is important that the total system be understood before recommending a treatment program. This includes knowledge of steam purity and the system needs for steam quality, as well as the effects of known contaminants on the process.

[1] For a more in-depth coverage of corrosion failures in boilers, refer to Dillon, J.J., Desch, P.B., Lai. T.S., Flynn, D.J., ed, *The NALCO Guide to Boiler Failure Analysis*, 2nd ed. McGraw-Hill, New York, NY, 2011.

[2] Consensus on Operating Practices for the Control of Feedwater and Boiler Water Chemistry in Modern Industrial Boilers, ASME, 1994.

CHAPTER 12

Turbines

Steam turbines are the workhorse in power plants as well as in industrial steam systems. The major use of steam is motive power, and this is the sole use in the utility industry. Even in moderate-sized industrial plants where the chief reason for generating steam is for process requirements, steam may be put through a turbine at high pressure, with the exhaust steam then being used for process needs. Turbines are the prime movers because they are compact and efficient. These prime movers may be used for direct drive of pumps, compressors, and other mechanical devices, or they may be connected to a generator to supply electrical energy.

Turbine Mechanics

In a steam turbine, the working fluid (in this case steam at high temperature and pressure) contains potential energy. The potential energy of the working fluid is converted into mechanical work through expansion in a nozzle and impact and/or reaction with a blade, and the mechanical work of many sets of blades attached to a shaft produces rotational power.

Water is converted to steam by the application of heat. As heat is supplied to water, temperature increases until boiling occurs [212°F (100°C) at atmospheric pressure]. At the boiling point, temperature remains constant until all water is converted to vapor (saturated steam). Although it requires only 1 Btu/lb for each degree Fahrenheit of temperature increase [4.18 kJ/(kg · °C)] to the boiling point, 970 Btu/lb (2255 kJ/kg) are required to change water at 212°F (100°C) to saturated steam. If the pressure of the boiler water is increased, the boiling point also increases, requiring application of still more energy. Steam at higher pressure has a higher temperature and contains more energy. As pressure increases, the amount of heat required to raise water to the boiling point increases, while the amount of heat necessary to vaporize the water decreases. Eventually at a pressure of 3200.1 psia (22.1 MPaa) and 705.1°F (373.9°C), water turns to steam without boiling; this is called the critical point. Turbines that operate at temperatures and pressures above the critical point are called supercritical units.

The problem with saturated steam, regarding turbines, is that it can contain water droplets, which can cause friction losses, erosion, and other problems. To dry saturated steam after vaporization, additional heat may be added to the steam, increasing its temperature; this process is called superheating. The enthalpy (potential energy) of steam increases by the amount of heat added. Superheating not only increases energy content, but also permits transporting steam through piping with less condensation.

The term enthalpy denotes the heat content of water or steam expressed in Btu/lb (kJ/kg). Enthalpy is a measure of the potential energy in the fluid. Steam tables have been developed to relate the properties of steam and water at various temperatures and pressures, and are available from the American Society of Mechanical Engineers (ASME) and other industry sources. Steam data can also be organized graphically in what is known as a Mollier chart.

To convert the steam's energy into work, steam must go through a thermodynamic fluid cycle that combines expansion, compression, heat input, and heat rejection. Steam turbines are based on the Rankine cycle (Fig. 12.1). At the end of the cycle, condensate is simply pumped back to the boiler to begin the cycle again. The role of the steam turbine is to expand the steam. As it expands, or drops in pressure, through a small opening or nozzle, it accelerates and forms a high-speed jet. Harnessing this momentum in a rotating blade provides mechanical work.

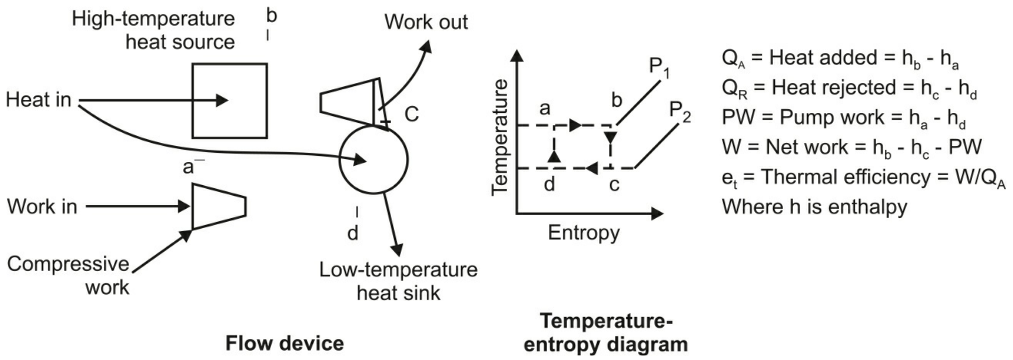

FIGURE 12.1 Rankine cycle. (*Courtesy of POWER Magazine, all rights reserved*.)

Turbines are fundamentally classified as impulse or reaction type based on how the steam expands through a nozzle and impacts a blade. In the simple single-stage turbine, steam is directed through a series of carefully shaped nozzles onto blades, or buckets, fixed at the circumference of the disk attached to the turbine shaft. This is known as the impulse stage. As steam leaves the rotating blades, a second set of stationary nozzles may be used to collect it and redirect it onto a second set of blades, or buckets, in which case the second set of nozzles and blades is called a reaction stage. Under ideal conditions, the steam jet does the most work when the blade speed is half the steam speed. Most turbines contain multiple stages, in practice, combining impulse and reaction stages. A simple single-stage turbine is shown in Figs. 12.2 and 12.3. A multiple-stage utility turbine is shown in Fig. 12.4.

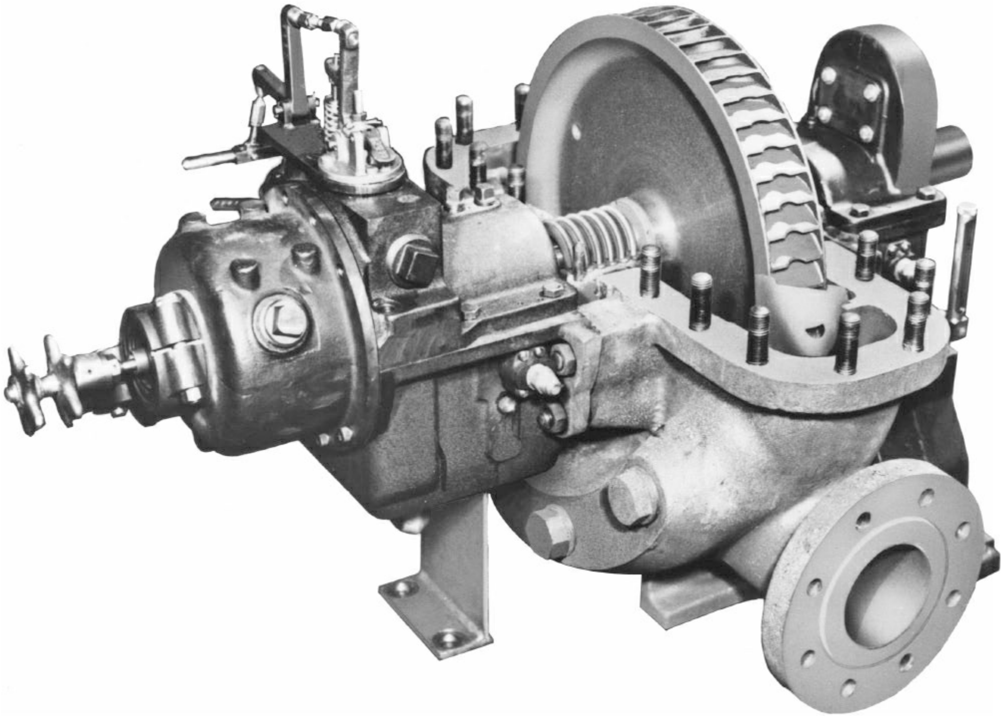

FIGURE 12.2 Simple solid wheel turbine commonly used to drive auxiliary equipment such as boiler feedwater pumps and rotary compressors.

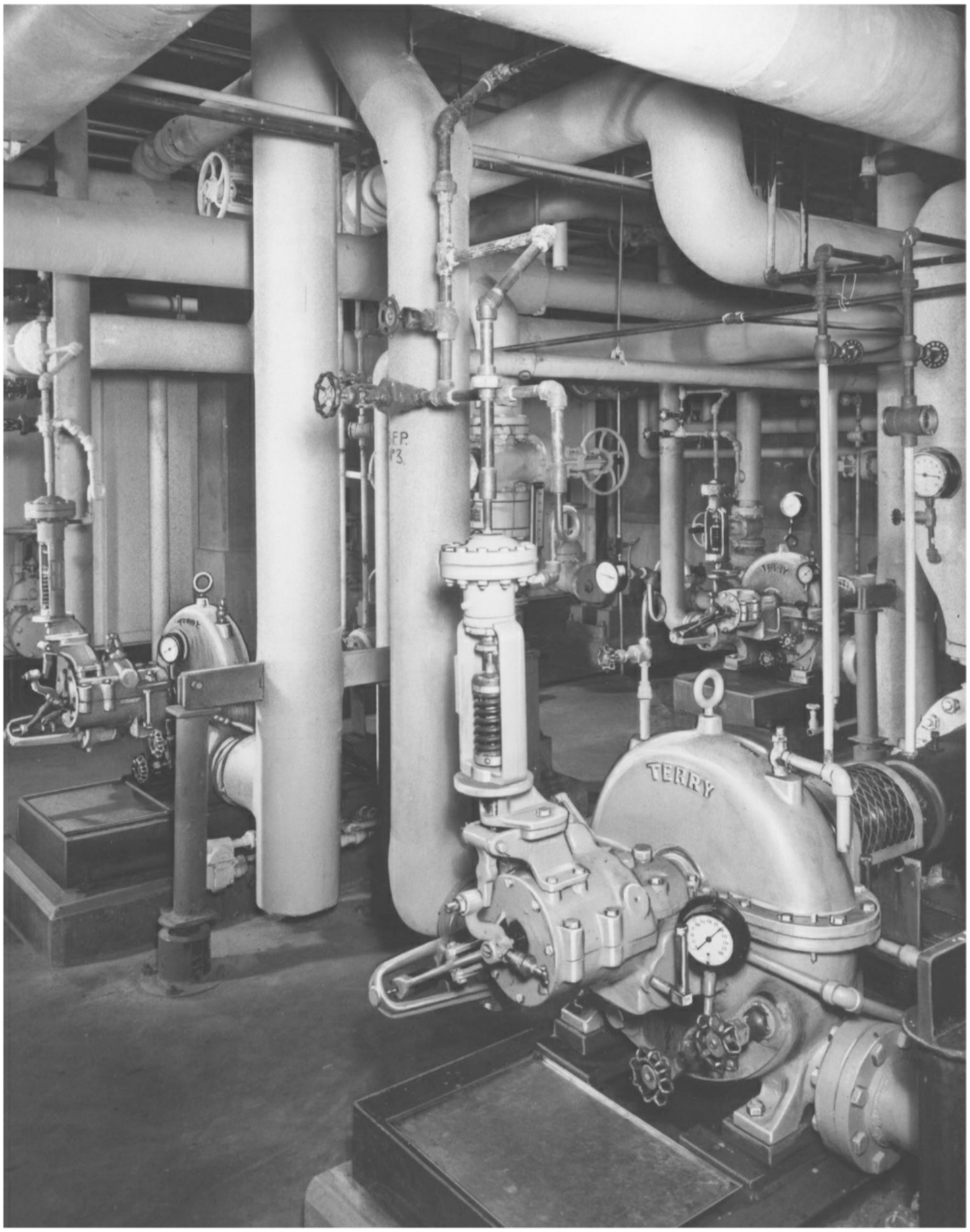

FIGURE 12.3 A typical plant installation of a single-stage turbine. (*From Power Special Report, "Steam Turbines," June 1962, Courtesy of Terry Corporation*.)

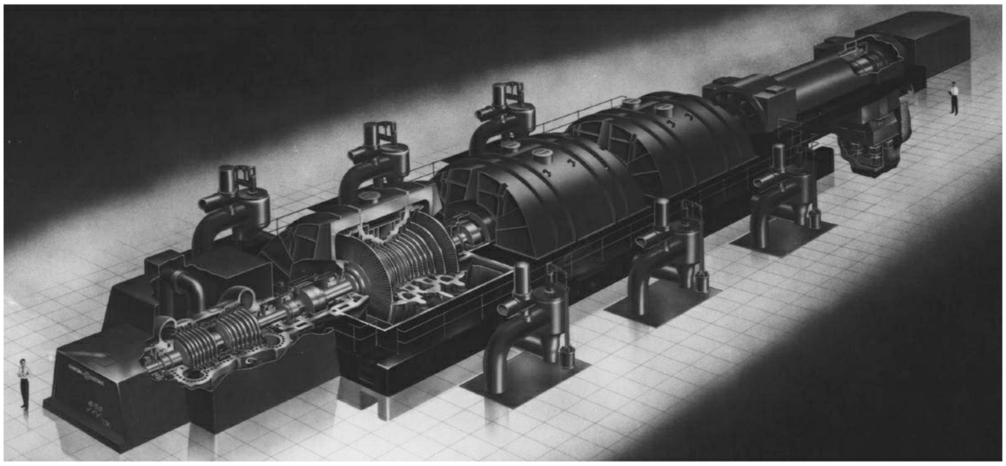

FIGURE 12.4 Large turbogenerator typical of nuclear power plants. Cutaway section shows high-pressure and low-pressure turbine blades. (*From Power Special Report, "Steam Turbines," June 1962, Courtesy of General Electric Company*.)

There are two basic categories of steam turbine operation: condensing, when exhaust steam discharges to a condenser at subatmospheric pressure and noncondensing, where steam exhausts into process steam headers under pressure. In the condensing turbine application, a vacuum is maintained in the condenser by steam-jet air ejectors or a mechanical vacuum pump. Shaft-sealing steam is applied to the turbine glands to prevent air from entering the seals and destroying the vacuum.

Turbine operation and designation are further classified as to the flow of steam through the turbine; flow patterns include straight flow, reheat, and extraction. In straight flow systems (Fig. 12.5), steam is directed by nozzles through the entire bank of turbine stages to exhaust. Reheat turbines, most commonly used in the electric utility industry, (Fig. 12.6) gain efficiency by discharging the main steam flow at one (single reheat) or two (double reheat) intermediate stages for reheat in the boiler, with that high temperature steam being returned to the next stage of the turbine for further expansion. In extraction turbines, steam is extracted from the main steam flow at one or more points for process use, with the balance passing through to exhaust (Fig. 12.7). Steam turbines come in a wide range of sizes. Capacities begin at less than 0.75 kW (1 hp) and extend up to more than 1300 MW for generator drives in the largest central electric generating stations. Larger turbines may have two shafts, side by side, driving two generators, known as cross compound units.

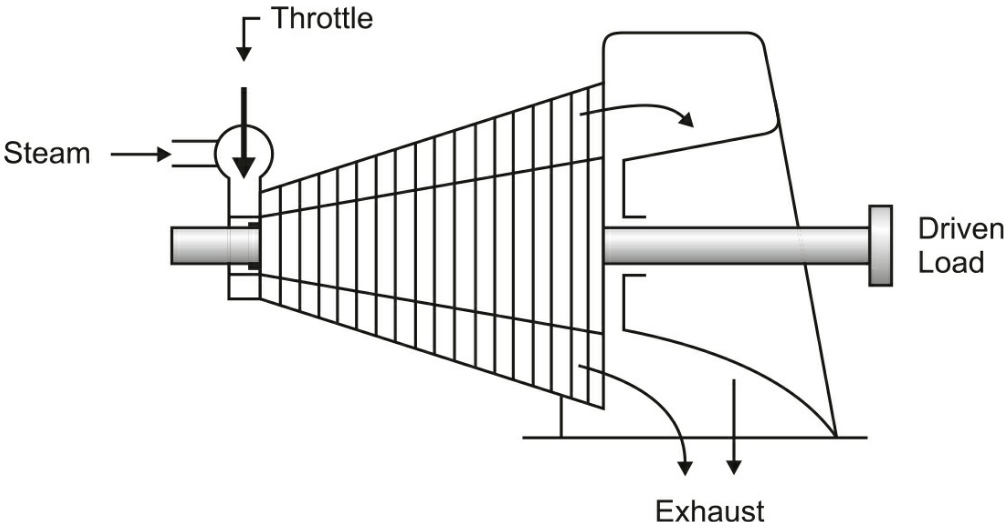

FIGURE 12.5 Straight-flow turbine. (*From Power Special Report. "Steam Turbines," June 1962*.)

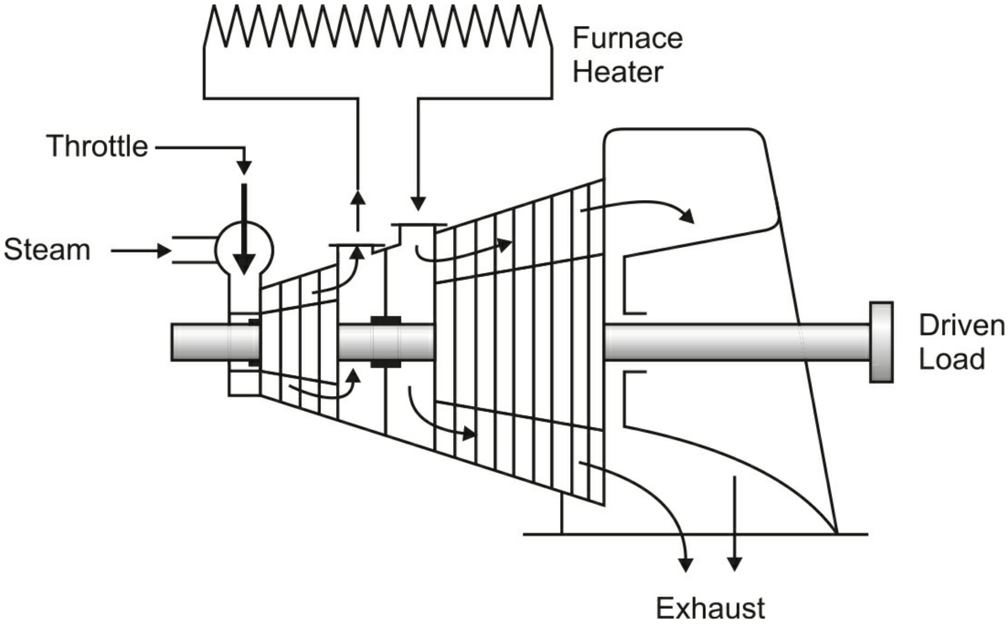

FIGURE 12.6 Reheat turbine. (*From Power Special Report. "Steam Turbines," June 1962*.)

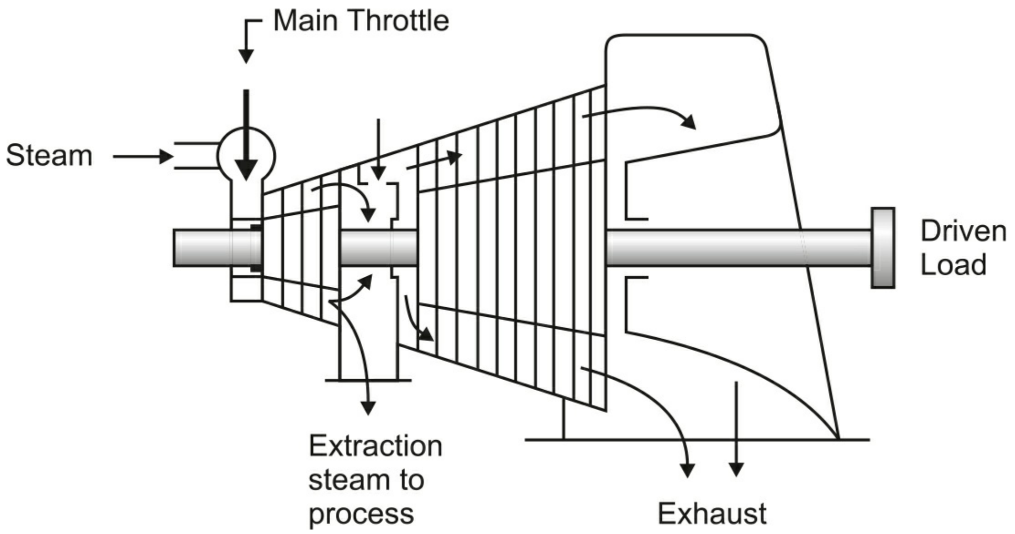

FIGURE 12.7 Single automatic extraction turbine.

Turbine Problem Areas

Solid particle erosion (SPE) of high-pressure (h-p) and intermediate-pressure (i-p) turbine internals, particularly blades and nozzles, is a common problem for boilers that produce steam at temperatures above 900°F (482°C). The common low-chromium alloy boiler materials, used in superheater and reheater tubes, headers, and piping forms a high-temperature oxide in service. This oxide scale can exfoliate from boiler tubes and steam leads once a critical thickness is reached and becomes entrained in the steam flow to the turbine, eroding components in the steam path. Temperature changes associated with startup, shutdown, and load cycling service, typically provide stresses on the oxide layer relative to the base material to initiate exfoliation. The effects of SPE include efficiency losses and susceptibility of damaged components to the possibility of mechanical failure and catastrophic loss.

Another troublesome type of turbine problem is related to the accumulation of material on turbine blading. This can be due to mechanical carryover of boiler water and its associated constituents into the steam or to the vaporous transport of selected species out of the boiler water into the steam. Deposits in the inlet high-pressure end of the turbine generally affect steam throughput. This is typically the result of high levels of mechanical carryover out of the boiler for most industrial turbine installations. Deposits can also cause vibration problems in the turbine and impair control valve operation.

For electric utility boiler systems operating above 2400 psig (16.5 MPag) drum pressure, copper oxide in its more oxidized form (CuO), which has a significant vaporous solubility in saturated steam, can result in deposits in the high-pressure turbine, restricting unit capacity. Strict control of feedwater oxidation-reduction potential (ORP) can minimize this transport of copper. Silica is the other boiler water constituent that has appreciable vaporous solubility in saturated steam above 600 psig (4.1 MPag), and must be limited in concentration in the boiler water to avoid vaporous transport to the turbine and subsequent deposition (typically in lower-pressure stages).

Lesser levels of impurities in the steam, but still above the solubility limit for those constituents in the phase transition zone (PTZ) of the low-pressure turbine section, can lead to deposition and corrosion problems. Acceptable steam purity for an industrial condensing steam turbine is typically less than 10 µg/L sodium in the steam and less than 20 µg/L sodium in the steam for an industrial backpressure turbine. Some turbines are more sensitive to deposition than others, and new turbine installations may have even more restrictive steam purity guarantee limits. Measurement of the sodium concentration in steam is commonly used as a method of determining steam purity. Sodium is a common element in boiler water and online instrumentation in the form of a sodium selective ion electrode is capable of reliably measuring sodium to sub µg/L levels.

Stress corrosion cracking (SCC) and corrosion fatigue are the two most common potential failure mechanisms associated with inorganic impurities (typically chlorides, sulfates, and caustic) in steam. The extent of the problem depends greatly on the purity of the steam and the blading and blading attachment design details. Most susceptible are the L-1 and L-0 (last stage) (Fig. 12.8). The transition between dry and wet steam, formerly known as the Willson line, now termed as PTZ, occurs here. The possible effects on the turbine of organic contaminants in steam are not nearly as well understood and are currently the subject of research activities in the industry.

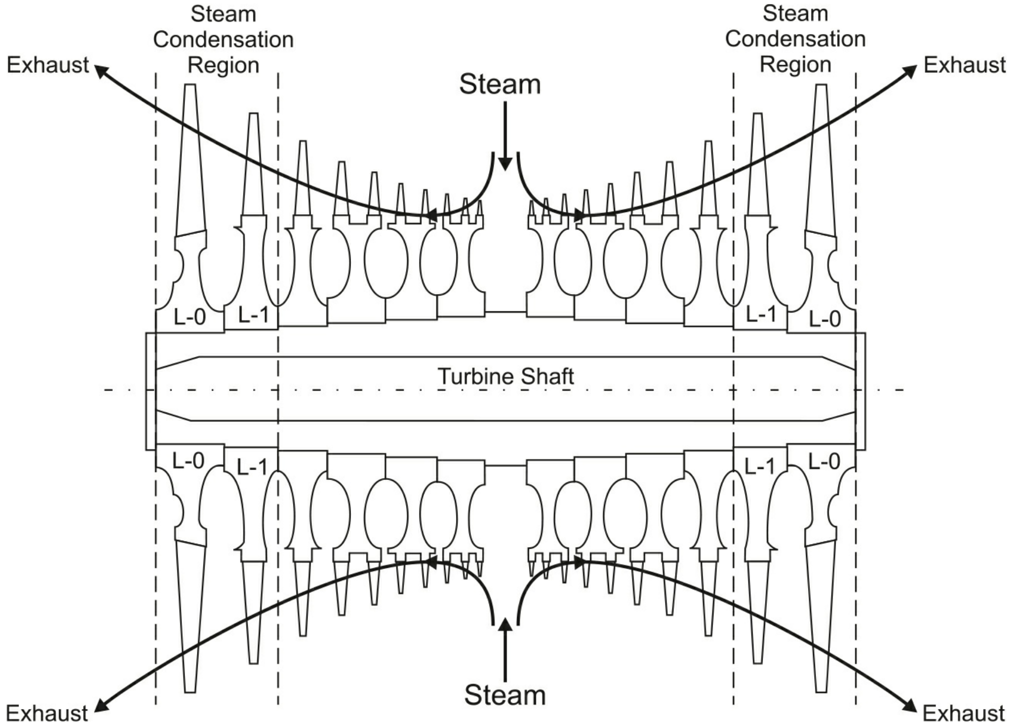

FIGURE 12.8 Illustration of the L-1 and L-0 placement on a turbine. (*Courtesy of POWER Magazine, all rights reserved*.)

Chemical compounds precipitate and deposit, when their concentration in superheated steam exceeds their solubility. Since solubility in dry steam decreases as steam expands, this mechanism is most common on components operating near the dry/wet transition (PTZ). In steady-state operation, deposition from dry steam involves three simultaneous processes: precipitation from expanding steam, deposition on a surface, and erosion of the deposit. Under load change, shutdown, and startup conditions, a deposit can be washed away by moisture. When steam composition changes from higher to lower concentration, a deposited salt can start dissolving back into dry steam and be carried away. A deposit can also be physically dislodged from surfaces and transported further forward into the steam system.

For some time, the turbine corrosion issues (stress corrosion cracking and corrosion fatigue) in the PTZ were thought to be associated with the online steam purity conditions and turbine operation. More recent work though, has shown that the corrosion mechanisms are initiated during out-of-service conditions when the system is exposed to moisture or humidity and oxygen at which time pitting may occur. These are then propagated into the cracking phenomena in subsequent operation. The current recommendation to minimize this potential damage mechanism is to apply a controlled out of service environment for the turbine via continual nitrogen purging or the application of a dehumidified air protection system.

Control of impurity sources, adequate treatment to remove impurities, and proper sampling and chemical analysis are essential to corrosion control. Chemistry control is one of the most important requirements during operation. In particular, direct analysis and control of steam chemistry is necessary, because boiler water specifications do not guarantee acceptable turbine steam.

Finally, smaller steam turbines (Figs. 12.9 and 12.10) are used to drive critical process equipment, including pumps, compressors, fans, and paper machines. Efficient mechanical drives are critical to an optimized steam system and plant energy balance. High steam temperatures, pressures, and speeds characterize turbines for mechanical drives. Improper steam purity can similarly adversely affect their availability and reliability.

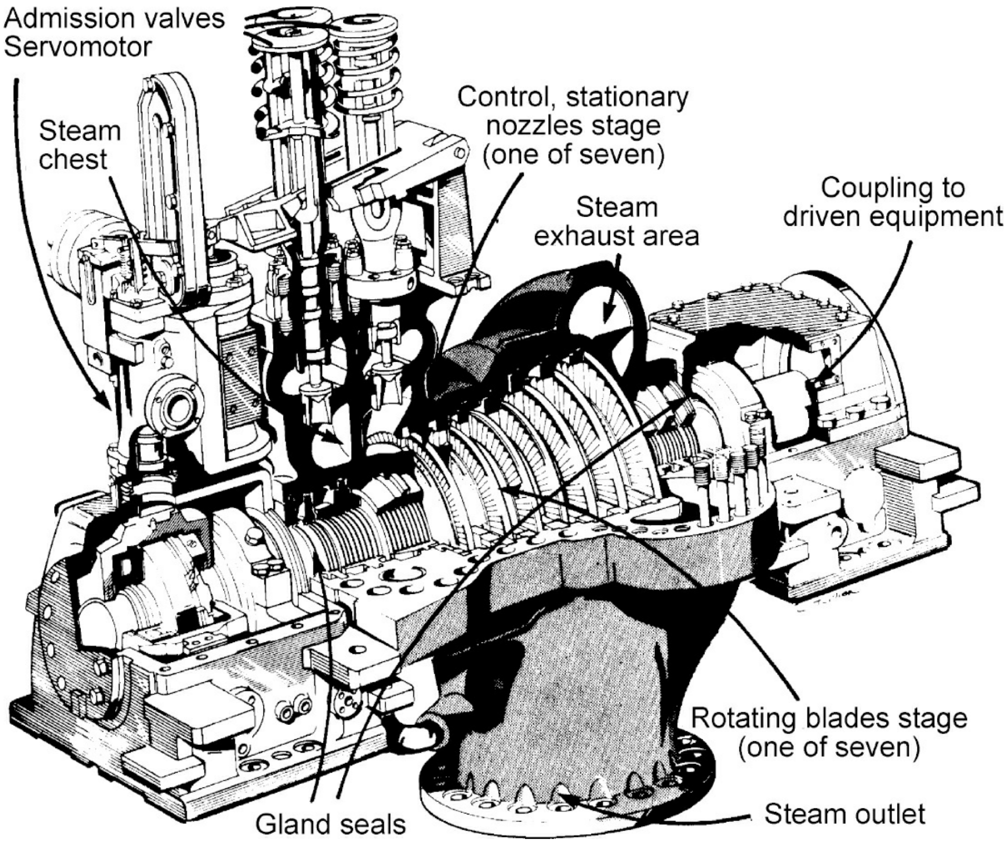

FIGURE 12.9 A backpressure multistage steam turbine. (*Courtesy of POWER Magazine, all rights reserved*.)

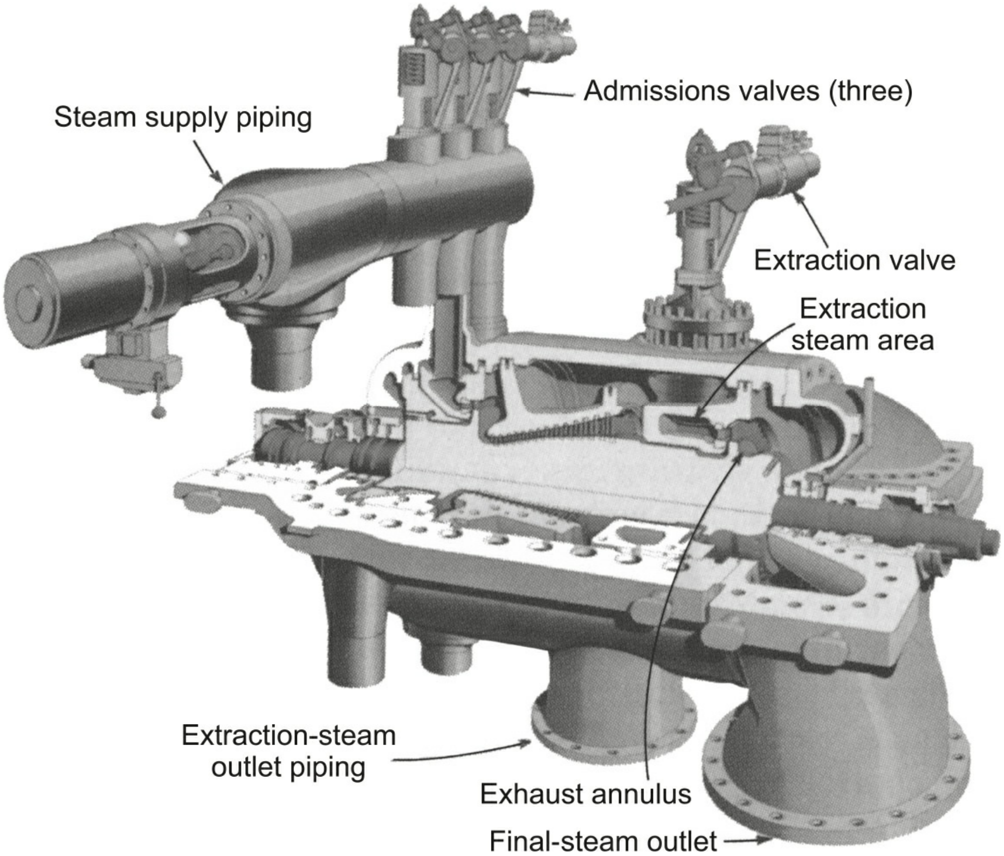

FIGURE 12.10 A single-extraction multistage steam backpressure turbine. (*Courtesy of POWER Magazine, all rights reserved*.)

In mechanical drive applications, steam turbines compete with electric motors. Advantages commonly attributed to turbines include: flexibility to use multiple inlet and exhaust pressure levels, inherent variable speed operation, operation independent of electric power supply, and spark-proof controls for hazardous fluid duty. The relative value of thermal-to-electric energy determines the motor/turbine selection decision.

CHAPTER 13

Condensate Systems

A primary objective in the successful operation of any steam generating system is to maximize its overall efficiency and reliability, while minimizing problems related to water and steam purity. One of the greatest factors in achieving this objective is the amount and purity of condensate returned to the boiler as feedwater. Returned condensate, being condensed steam, is typically free of impurities and has a relatively high heat content, making it ideal, both economically and technically, for boiler feedwater.

Economically, the more condensate returned, the less makeup water required, thereby saving on both water and feedwater pretreatment costs. The high purity of condensate allows the boiler to operate at higher cycles of concentration while maintaining conductivity standards, thereby reducing costly water and energy losses to boiler blowdown. The higher heat content of condensate [158 Btu/lb at 190°F (367 kJ/kg at 88°C)] as compared to makeup water [28 Btu/lb at 60°F (65 kJ/kg at 16°C)] directly reduces the fuel requirements of the boiler to convert feedwater into steam.

Technically, the high purity of condensate reduces the overall scale-forming tendency of boiler feedwater, regardless of the sophistication of the makeup water pretreatment system. This results in cleaner heat transfer surfaces and optimal heat transfer rates. Higher purity feedwater reduces the possibility of boiler tube failure due to excessive scaling.

To realize the benefits of a condensate return system, a program of corrosion control must be implemented. Left untreated or treated improperly, condensate can become very corrosive to plant piping and equipment. The resulting products of corrosion can enter the feedwater and form harmful, tenacious deposits on boiler heat transfer surfaces. The lack of condensate corrosion control can ultimately result in the loss of heat transfer efficiency and ruptured boiler tubes, a leading cause of unscheduled plant shutdowns.

Causes of Condensate System Corrosion

It is a myth that pure condensed steam is noncorrosive to most metals. Condensate formed from extremely pure steam has a conductivity of less than 1 µS/cm and a pH of 6.5 to 7.0. These are the characteristics of pure water. At a pH of 6.5 to 7.0, condensate is very aggressive to most metals. The presence of very small amounts of contaminants in the steam or leaking into the liquid condensate can further depress the pH and accelerate the corrosion rate of most ferrous and nonferrous metals.

The primary contaminants that lead to increased condensate corrosion are gases carried in the steam from the boiler. These gases dissolve in the condensate to form a solution corrosive to most metals. Carbon dioxide and oxygen are the gases most corrosive to ferrous metals; the combination of ammonia and oxygen poses the greatest corrosive threat to copper alloys. In certain instances, sulfur dioxide, hydrogen sulfide, and organic acids result in very corrosive condensate.

Carbon Dioxide

The gas most commonly associated with condensate corrosion is carbon dioxide (CO_2). Although CO_2 can be found in many waters in the free state, it is normally removed through pretreatment and deaeration. The major source of CO_2 in the steam is the thermal breakdown of bicarbonate (HCO_3^-) and carbonate (CO_3^{-2}) alkalinity present in the feedwater. At boiler temperatures and pressures, the following alkalinity reactions occur:

$$2NaHCO_3 \rightarrow Na_2CO_3 + CO_2\uparrow + H_2O \tag{13.1}$$

$$Na_2CO_3 + H_2O \rightarrow 2NaOH + CO_2\uparrow \tag{13.2}$$

The breakdown of bicarbonate [Eq. (13.1)] proceeds 100% to completion. Carbonate breakdown [Eq. (13.2)] proceeds from 10 to 90% to completion, depending on the temperature, pressure, and holding time of the boiler. The CO_2 liberated in both reactions exits the boiler with the steam.

Carbon dioxide is not harmful until it dissolves in the condensate. As it dissolves, it forms carbonic acid (H_2CO_3):

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \quad (13.3)$$

The extent to which carbon dioxide dissolves is predicted by Henry's law, which states that the quantity of gas that can dissolve in a liquid is proportional to its partial pressure in the contacting vapor or gas phase. The solubility of CO_2 is also influenced by temperature and pressure, since gases are less soluble in liquid as the temperature approaches or exceeds the boiling point. Finally, CO_2 solubility is influenced by pH, since pH determines whether the CO_2 remains as a gas (with a vapor pressure) or converts to the bicarbonate salt (without a vapor pressure). All together, these three principles determine the vapor/liquid (*V/L*) distribution ratio for CO_2 at the specific conditions present. (*V/L* ratios will be discussed later with neutralizing amines.)

Since condensate is extremely pure, even small quantities of carbonic acid, a relatively weak acid, can significantly lower condensate pH and correspondingly increase its corrosivity. Figure 13.1 shows that as little as 1 mg/L of CO_2 in the steam can depress condensate pH from 7.0 to 5.5 at typical condensate temperatures. It is apparent that high alkalinity feedwater will produce very corrosive condensate.

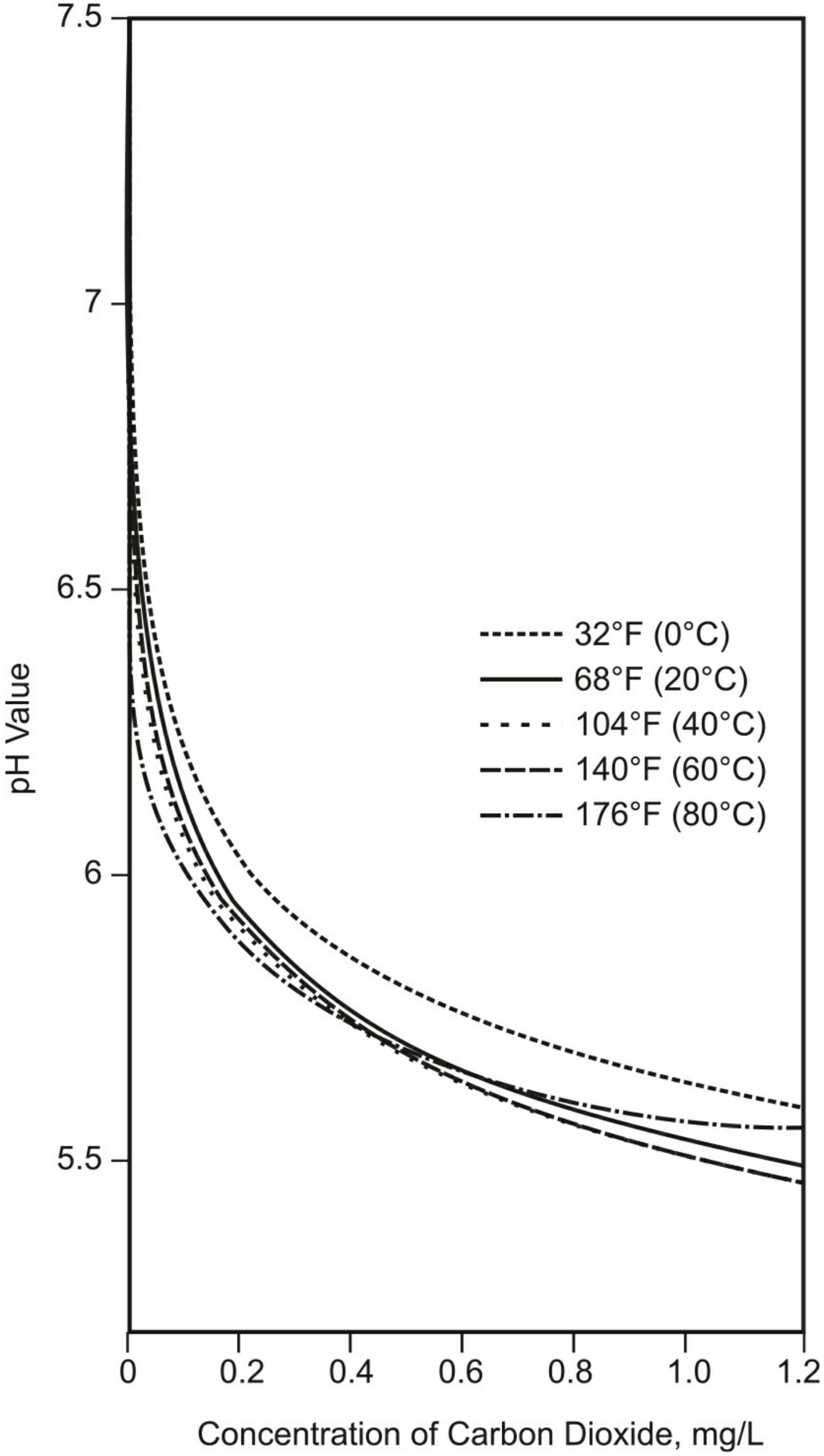
7.5
7
6.5
6
5.5
pH Value
32°F (0°C)
68°F (20°C)
104°F (40°C)
140°F (60°C)
176°F (80°C)
0
0.2
0.4
0.6
0.8
1.0
1.2
Concentration of Carbon Dioxide, mg/L

FIGURE 13.1 pH versus CO_2 concentration in pure water at various temperatures.

The corrosion reaction of carbonic acid on iron produces ferrous bicarbonate [$Fe(HCO_3)_2$] and hydrogen gas:

$$Fe + 2H^+ + 2HCO_3^{-2} \rightarrow Fe(HCO_3)_2 + H_2\uparrow \tag{13.4}$$

The ferrous bicarbonate is highly soluble and has no passivating effect. It can be carried away with the condensate, leaving behind an area of obvious metal loss. The ferrous bicarbonate is not particularly stable, and various secondary reactions are likely to take place, resulting in the formation of ferrous and ferric oxides, hydroxides, and carbonates.

Carbonic acid attack is characterized by a thinning or grooving of metal surfaces in contact with the corrosive condensate. In the absence of oxygen, carbonic acid generally causes a rather smooth surface, where the iron has been dissolved away as shown in Fig. 13.2.

FIGURE 13.2 Carbon dioxide corrosion.

Carbon dioxide in the steam can be decreased by removal of bicarbonate and carbonate alkalinity in the makeup water. This can be accomplished by a well-controlled lime softening program or by dealkalization, demineralization, reverse osmosis, or degasification processes. (A small amount may be lost by deaeration, depending on makeup water pH.) These processes are never 100% complete, so some bicarbonate/carbonate is always present in the makeup water, the actual amount depending on the pretreatment process. As a result, some CO_2 is always present in the steam.

Estimating the Amount of Carbon Dioxide in Steam

There is no accurate means of determining CO_2 in steam. Analytical field methods only detect free CO_2 (uncombined with amines or ammonia), and laboratory methods require fixing a sample and transporting it offsite for analysis. The sample is easily contaminated during both steps. Various equations have been developed for the estimation of CO_2. All of them generally estimate the correct range, although some might end up closer to the actual concentration than others.

Oxygen

Oxygen (O_2) is present in most makeup waters, but is usually reduced before entering the boiler by deaeration or chemical oxygen scavenging. If oxygen is not removed, it will flash from the boiler water and be carried along with the steam. This is probably the most critical source of oxygen in the condensate system. The oxygen flashed with the steam is present when condensation first occurs—the time when the metal is most susceptible to attack. Fortunately, large amounts of oxygen are easily kept from operating systems by mechanically deaerating the feedwater and then adding chemical oxygen scavengers.

The major source of condensate oxygen, however, is air inleakage into the system itself. Oxygen concentrations greater than 50 μg/L are typical of systems with air inleakage. The final concentration is largely dependent on the temperature of the condensate.

Oxygen can leak into a system via absorption into the condensate in atmospheric systems (vented receiver tanks), with raw water inleakage, and as air drawn in through small leaks, when the system is under a vacuum or operates intermittently and pulls a vacuum as the equipment cools (e.g., at threaded joints, heat exchangers, faulty steam traps, packing glands, and vented receivers). Severe pitting caused by oxygen attack can frequently be found at or just below the liquid surface in partially filled vessels and pipes, and at points above the surface where condensate droplets are formed. Although chemical solutions to this problem exist, air inleakage should be solved first by making the required system repairs.

Oxygen in condensate systems can cause severe pitting corrosion (Fig. 13.3). These oxygen pits can rapidly corrode through metal surfaces, greatly reducing equipment life and contaminating feedwater with undesirable corrosion products. Oxygen in the condensate reacts with iron to form ferric hydroxide:

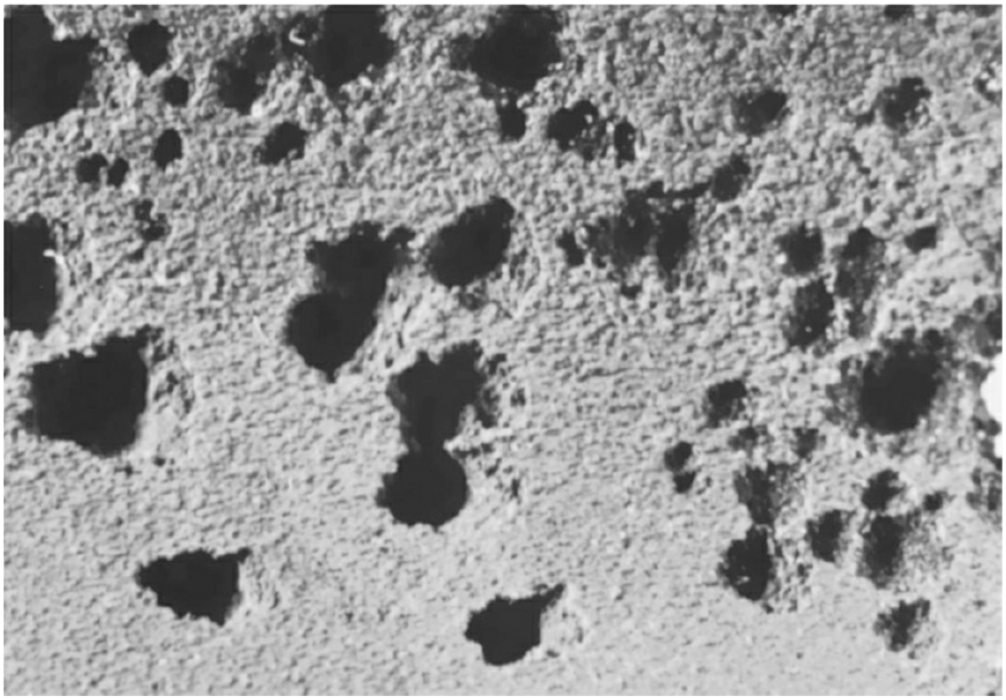

FIGURE 13.3 Oxygen pitting.

$$4\text{Fe} + 6\text{H}_2\text{O} + 3\text{O}_2 \rightarrow 4\text{Fe(OH)}_3 \tag{13.5}$$

The ferric hydroxide then generally reverts in the condensate to form particulate iron oxide:

$$2\text{Fe(OH)}_3 \rightarrow \text{Fe}_2\text{O}_3 + 3\text{H}_2\text{O} \tag{13.6}$$

The iron oxide may further oxidize and is usually found in deposits on heat transfer surfaces as combinations of FeO, Fe_2O_3, and Fe_3O_4. These oxides often precipitate and settle in the condensate system in areas of low flow or reduced pressure. Deposits of this type have been known to build up to the point where condensate flow is severely restricted and even blocked.

When corrosion is controlled by the diffusion of oxygen, the corrosion rate at a given oxygen concentration approximately doubles for every 54°F (30°C) rise in temperature.

The corrosion rate in an open vessel where dissolved oxygen is allowed to escape, increases to about 176°F (80°C) and then falls to a very low value at the boiling point of water (Fig. 13.4). The corrosion rate decrease above 176°F (80°C) is related to the significant decrease of oxygen solubility in water as the temperature approaches the boiling point. In a closed or unvented system, oxygen cannot escape, and the corrosion rate continues to increase with increasing temperature, until the corrosion process has consumed all oxygen.

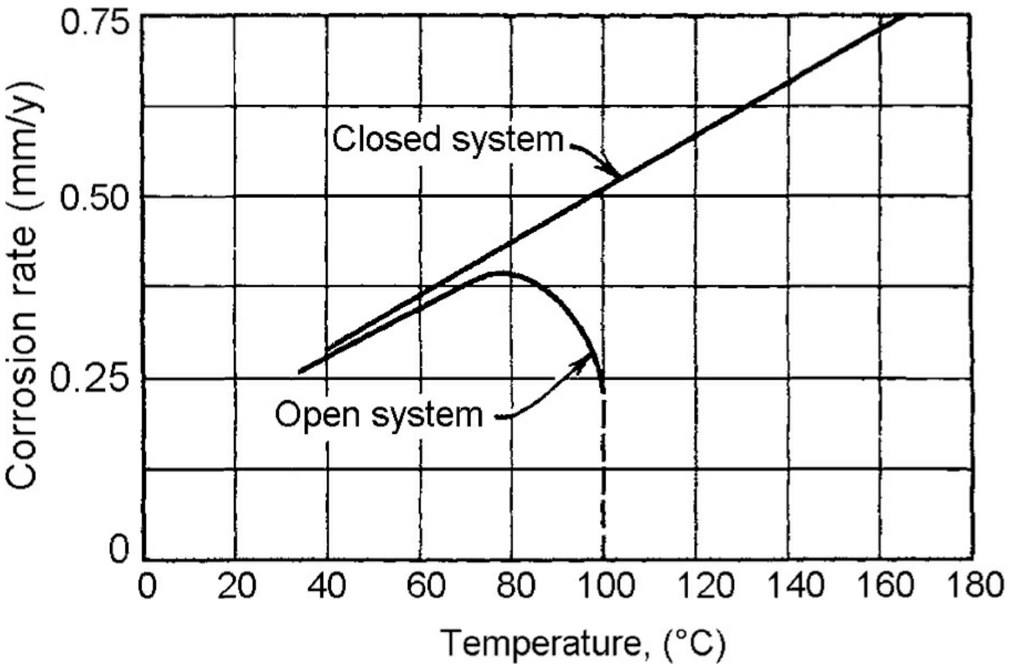

FIGURE 13.4 Effect of temperature on corrosion of iron in water containing dissolved oxygen (1 ipy = 1000 mpy = 25.4 mm/y).

At 140°F (60°C), oxygen is 6 to 10 times more corrosive to iron than the molar equivalent concentration of carbon dioxide. At pH levels below 6.0, corrosion of mild steel appears as a general metal loss with rough surfaces and some pitting present. At higher pH, the characteristic pitting attack is more noticeable.

Oxygen is also aggressive toward copper and its alloys. Oxygen can combine directly with copper to form cuprous or more often cupric oxide. Cupric oxide (CuO) is dark and provides a somewhat protective layer, preventing further attack. Cuprous oxide (Cu_2O) is red and indicates active corrosion.

In the presence of oxygen at pH above 9.2, any copper complexing agent such as ammonia can destroy the protective cupric oxide film, exposing fresh metal surface to further attack. Control of ammonia is the first line of defense against oxygen attack on copper.

Carbon Dioxide Plus Oxygen

The corrosion reaction of carbonic acid with iron is pH dependent, resulting in the evolution of hydrogen and the formation of ferrous bicarbonate. Experience has shown that when oxygen is present along with the carbon dioxide in the condensate, corrosion rates are greatly accelerated. In the presence of both carbon dioxide and oxygen, two cathodic reactions are now possible: evolution of hydrogen [Eq. (13.4)] and reduction of oxygen [Eqs. (13.7) and (13.8)], the latter being a faster reaction:

$$2Fe + O_2 + 4H^+ \rightarrow 2Fe^{+2} + 2H_2O \tag{13.7}$$

$$4Fe^{+2} + O_2 + 4H^+ \rightarrow 4Fe^{+3} + 2H_2O \tag{13.8}$$

The combination of carbon dioxide and oxygen appears to accelerate corrosion by 10 to 40% more than the corrosion rate occurring by either gas alone. Additionally, oxygen may react with existing corrosion products and further perpetuate the process by releasing CO_2. An example of this is shown by the following reaction:

$$4Fe(HCO_3)_2 + O_2 \rightarrow 2Fe_2O_3 + 4H_2O + 8CO_2\uparrow \tag{13.9}$$

The overall corrosion can be very severe and appear as worming or surface roughness, as shown in Fig. 13.5. At pH less than 6.0, corrosion is attributed mainly to the carbon dioxide content. Where oxygen is also present, it acts to increase the rate of acidic attack. The type of oxygen pit developed is influenced by the condensate pH. Oxygen pitting begins at the weak points in the iron oxide film or at sites where it is damaged. At low pH, the iron oxide film is not very protective, so the pits tend to be large. As the condensate pH rises, the iron oxide film becomes more protective, and the pits tend to be smaller. In the pH range of 6 to 8, with oxygen concentrations between 0.5 and 4.0 mg/L, the rate of general attack is proportional to the oxygen concentration.

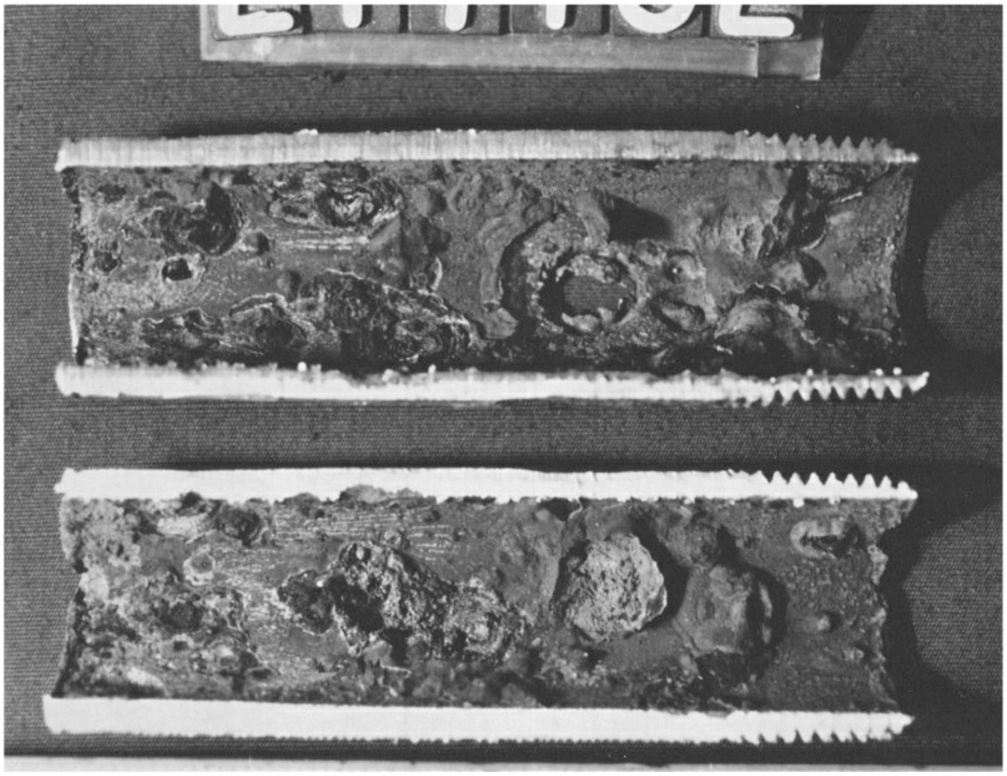

FIGURE 13.5 Internal surface of condensate line.

Ammonia

Ammonia enters the boiler system in a number of ways. It is present in some natural waters as the result of breakdown of organic materials. A greater number of city and municipal water departments are now using ammonia to stabilize chlorine as chloramine in order to obtain better biological control in the drinking water distribution system. Chloramines that pass through pretreatment systems and enter boiler feedwater generate ammonia. Another source of ammonia is chemical breakdown of boiler water additives such as hydrazine or hydrazine alternatives (e.g., carbohydrazide, diethylhydroxylamine, and methylethylketoxime), some polymers (e.g., acrylamide-based polymers), and amines [generally at temperatures above 850°F (454°C)]. Ammonia can also result from process contamination or intentional feed as condensate treatment.

Ammonia can reduce the corrosion of ferrous metals by neutralizing carbonic acid and raising the pH of the condensate. However, ammonia is corrosive to copper alloys in the presence of oxygen. The oxygen reacts with the copper to produce a copper oxide coating on the metal, which is rapidly dissolved by ammonia. This oxidation and dissolving reaction produces a soluble cupric-ammonia complex:

$$Cu + \tfrac{1}{2}O_2 \rightarrow CuO \qquad (13.10)$$

$$CuO + 4NH_3 + H_2O \rightarrow Cu(NH_3)_4^{+2} + 2OH^- \qquad (13.11)$$

This rapid creation and destruction of the copper oxide film results in a very destructive cycle, which is especially aggressive below pH 8.5 and above pH 9.2.

Table 13.1 shows the concentrations of ammonia and oxygen that can typically be tolerated in minimizing copper corrosion.

Dissolved Oxygen, µg/L	Maximum Allowable Ammonia, mg/L
0–20	0.5
21–50	0.3
Over 50	Any level may cause a problem

TABLE 13.1 Relationship of Oxygen and Ammonia

The main sources of ammonia present in a condensate system should be located and reduced or eliminated. Concentrations can sometimes be lowered by periodically discarding the aftercooler drips from the condenser steam jet air ejector. Ammonia is usually highly concentrated in these drains.

In systems with mixed metallurgy or insufficient sample points, a filming amine or Nalco ACT ® provide protection against ammonia, if the proper pH range is maintained.

Sulfur Dioxide and Hydrogen Sulfide

Catalyzed sodium sulfite (Na_2SO_3) is commonly used to scavenge dissolved oxygen from boiler feedwater following deaeration. While this treatment provides excellent oxygen removal, it has certain limitations, including a recommended boiler drum pressure limitation of 900 psig (6.2 MPag). Sodium sulfite begins to decompose at approximately 600 psig (4.1 MPag) to form sulfur dioxide (SO_2) and hydrogen sulfide (H_2S) gases, which are carried with the steam. The rate of decomposition increases rapidly above 900 psig (6.2 MPag):

$$Na_2SO_3 + H_2O \rightarrow SO_2\uparrow + 2NaOH \tag{13.12}$$

$$4Na_2SO_3 + 2H_2O \rightarrow 3Na_2SO_4 + 2NaOH + H_2S\uparrow \tag{13.13}$$

These gases dissolve in the condensate much in the same way as CO_2. However, the sulfurous acid (H_2SO_3) produced by SO_2 is considerably stronger than the carbonic acid produced by CO_2. Correspondingly, the acid neutralization becomes more difficult, and the corrosion process proceeds faster. Sulfur, sulfides, and H_2S are particularly corrosive to copper and its alloys. There is also indication that the presence of H_2S and SO_2 in the steam can cause stress corrosion cracking of copper and its alloys, especially in steam turbine condensers.

Process Contamination and Organic Acids

Aside from the various gases that can dissolve in the condensate from thermal breakdown or inleakage, condensate can become corrosive through process contamination. Because of the natural high purity of condensate, very small amounts of contaminant can render it extremely corrosive and unsuitable as feedwater. Process liquids, catalysts, cleaners, solvents, equipment and fabrication oils and lubricants, and condenser cooling water are all potential contaminants.

Process contaminants may be corrosive in their original state, or they may decompose to corrosive compounds in the boiler. Decomposition of organic molecules in the boiler water generally results in the formation of low molecular weight organic acids (e.g., acetic, formic, and glycolic acids) and carbon dioxide. These low molecular weight organic acids are volatile, although their volatility is relatively low compared to commonly used neutralizing amines. All are considerably stronger than carbonic acid and increase the amine demand in the condensate. They also consume alkalinity in the boiler water.

Another concern is contamination originating in jacketed reaction vessels. Reactors, mix tanks, blend tanks, and other reaction vessels are often surrounded by jackets or coils that can heat or cool the vessel and its contents during processing. This jacketed vessel, sometimes called an annular space heat exchanger, is typically an open space surrounding the vessel through which steam, cooling water, and other fluids flow. Condensate from these vessels is frequently contaminated by cooling water. Precautions should be taken to isolate reaction vessels in order to prevent contaminated condensate from returning to the boiler system.

Methods of Condensate Corrosion Inhibition

Effective corrosion control for a condensate system must include mechanical, operational, and chemical (MOC) aspects. Chemicals alone are not adequate or cost-effective.

Mechanically, the elimination of all avenues of air, water, and process inleakage is an essential part of system protection. Feedwater oxygen can be almost completely eliminated by mechanical deaeration plus the use of an oxygen scavenger. In addition, various pretreatment processes such as hot lime softening, dealkalization, demineralization, and reverse osmosis can be used to reduce makeup water bicarbonates and carbonates.

All equipment must be properly operated and maintained to achieve the desired results. Maximum condensate recovery for boiler feedwater reduces potential CO_2 generation and subsequent amine consumption and condensate corrosion. Good monitoring of pretreatment, feedwater, and condensate systems coupled with rapid response to upsets is essential for effective corrosion control.

However, even with excellent pretreatment and feedwater deaeration, chemical inhibitors are still necessary for complete protection. Chemically, four types of inhibitors are used for condensate corrosion control: neutralizing amines, filming amines, nonvolatile filming technology, and oxygen scavengers/metal passivators.

Neutralizing Amines

Neutralizing amines are volatile, alkaline compounds that are added to either the boiler feedwater or the steam supply systems. They function by volatilizing into the steam and redissolving in the condensate with the CO_2. The amines chemically neutralize carbonic acid, or any other acid, present in the system. They raise pH to a level at which the condensate is much less aggressive to the system metal.

Most commercially available neutralizing amine condensate treatments are blends of various amines. The blends offer combinations of certain characteristics that are unique to each amine. The characteristics of greatest importance when selecting amines are specific volatility (*V/L* ratio), basicity, acid neutralizing ability, thermal stability, and compliance with government regulations. Amine recycle may also be important. Each characteristic must be considered when selecting a condensate corrosion inhibitor program.

Volatility

Every gas in a condensate system has a specific volatility or vapor to liquid distribution ratio (*V/L*). The *V/L* distribution ratio is defined by:

$$\frac{V}{L} = \frac{V_{\text{conc}}}{L_{\text{conc}}} \tag{13.14}$$

where V_{conc} = concentration in the vapor or steam phase
L_{conc} = concentration in the liquid or condensate phase

The *V/L* distribution ratio indicates how much of the species will condense with the condensate or stay with the steam. For example, a *V/L* ratio of 4.0 indicates that 4.0 mg/L of amine must be present in the steam to get 1.0 mg/L in the condensate (5 mg/L total amine present). The higher the *V/L* ratio, the more amine will be present in the steam for each mg/L present in the liquid. The *V/L* ratio is applied at each point of condensation. To neutralize carbon dioxide, the amine must be present in the condensate as the CO_2 dissolves.

V/L ratios vary with pressure, temperature, pH, and other operating conditions. They do not depend on distance from a steam generator or boiler. Table 13.2 shows how the *V/L* ratio of three common neutralizing amines and carbon dioxide vary by pH. Table 13.3 shows how the *V/L* ratios of various amines vary by pressure for the pH range 7.5 to 9.5.

Pressure psig (kPag)	Cyclohexylamine		Diethylaminoethanol		Morpholine		Carbon Dioxide
	pH 7.5–9.5	pH 10–11.5	pH 7.5–9.5	pH 10–11.5	pH 7.5–9.5	pH 10–11.5	pH 7.5–9.5
10 (69)	2.7	13	2.2	4.1	0.4	0.4	3.0
150 (1034)	4.0	20	4.3	5.8	0.5	0.99	8.5

TABLE 13.2 *V*/*L* Ratios for Carbon Dioxide, Cyclohexylamine, Diethylaminoethanol, and Morpholine

Amine	Pressure, psig (kPag)				
	10 (69)	50 (345)	150 (1034)	600 (4137)	900 (6205)
Ammonia	3.0	6.7	7.0	5.0	4.3
Carbon dioxide	3.0	4.8	8.5*	15.8	99
Cyclohexylamine	2.7	3.0	4.0	10	6.6
Diethylaminoethanol	2.2	3.0	4.3	5.2	4.5
Morpholine	0.4	0.44	0.5	1.22	1.22

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*At 350 psig (2413 kPag)

TABLE 13.3 *V*/*L* Ratios of Various Neutralizing Amines Used in Boiler Systems (pH 7.5–9.5)

V/*L* distribution ratios are significant only when a phase separation occurs. For example, in a flash tank, condensate enters the vessel, but both condensate and steam exit the vessel. Low volatility amines such as morpholine tend to be present in greater concentration in the condensate exiting the flash tank. If morpholine alone were fed to the system, the condensate exiting the flash tank might have adequate protection, but the flashed steam could have a low pH when finally condensed. High volatility cyclohexylamine tends to be present at higher concentrations in the steam exiting the flash tank. If cyclohexylamine alone were fed to the system, the condensate exiting the flash tank would likely have adequate protection, whereas the flashed steam would have a higher pH (than with morpholine) at final condensation. This example illustrates the necessity of amine blends for adequate corrosion protection of the entire condensate system.

Any vented process unit or condensate receiver tank has a phase separation (release of some steam, CO_2, amines, and NH_3). A sample of condensate exiting a vented unit is often not representative of the condensate entering it. pH readings taken from these locations will typically be higher than the pH of the condensate entering the receiver, due to the loss of more CO_2 than amine or ammonia.

V/L ratios are not significant when total condensation occurs. In units with total condensation, all the carbon dioxide, amines, and ammonia in the steam entering a unit are dissolved into the condensate (no phase separation exists).

Basicity

Basicity is a measure of amine hydrolysis. Neutralizing amines used for condensate treatment are primary, secondary, or tertiary amines and can be represented by the general formula RNH_2, where R denotes an organic radical. Hydrolysis generates a captive hydroxide ion (OH^-), which is present in solution as long as the amine molecule is present [Eq. (13.15)]. In the neutralization process, the hydrolyzed amine reacts with the bicarbonate to form an amine bicarbonate salt [Eq. (13.16)]. Equation (13.3) is repeated here so that the full reaction can be seen. The OH^- group generated by amine hydrolysis reacts with the H^+ group from carbonic acid to form water [Eq. (13.16)].

$$RNH_2 + H_2O \rightleftharpoons RNH_3^+ + OH^- \tag{13.15}$$

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \tag{13.3}$$

$$RNH_3^+ + OH^- + H^+ + HCO_3^- \rightleftharpoons RNH_3HCO_3 + H_2O \tag{13.16}$$

The basicity of neutralizing amines varies. For example, cyclohexylamine is a much stronger base than morpholine. Table 13.4 shows basicity constants for various amines. Past a certain pH, additional quantities of the weaker neutralizing amines such as morpholine do little to further increase pH.

Amine	Molecular Weight	pKa
Ammonia	17	9.3
Cyclohexylamine	99	10.6
Diethylaminoethanol	117	9.6
Morpholine	87	8.4

TABLE 13.4 Basicity Constants and Molecular Weight for Common Neutralizing Amines

Acid Neutralizing Ability

Another very important aspect of amine selection is its acid neutralizing ability. This is the amount of amine required on a weight basis to neutralize one mole (44 g) of carbonic acid. This characteristic is dependent upon the equivalent weight of the amine. The net reaction shown by Eq. (13.16) goes to exhaustion of either amine or acid. The final pH is then determined by hydrolysis of the left over component. On a mass basis, lower molecular weight amines neutralize more carbonic acid than higher molecular weight amines.

Figure 13.6 shows a graphic representation of the combined effects of acid neutralizing ability and basicity.

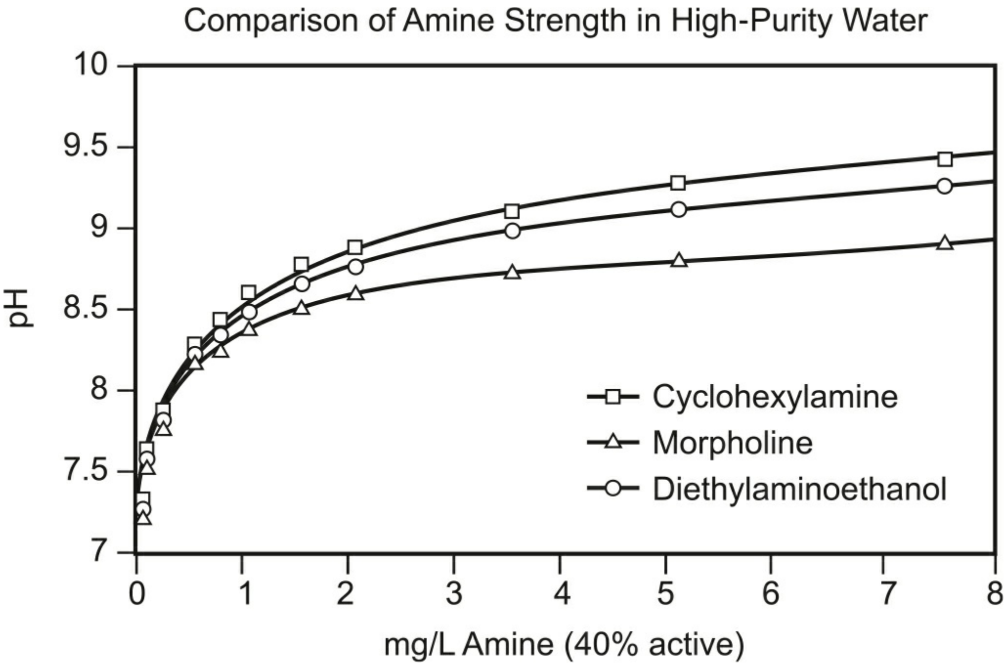

FIGURE 13.6 pH effect of acid neutralizing ability and basicity of common neutralizing amines.

Thermal Stability

All organic molecules, including amines, have specific temperature limitations, above which they thermally decompose. Most water treatment chemicals commonly used in boiler systems have been chosen for their exceptional thermal stability, yet all eventually break down in the boiler system given sufficient heat and holding time.

Amine thermal stability is primarily dependent on time at temperature, but system oxygen can also be a factor. The superheater is typically the location of highest heat within the boiler system. Because exposure time to superheat temperatures is extremely short, many amines can be used at temperatures above their known decomposition temperatures without appreciable loss. Amines used in systems with reheat have significantly more exposure time at high temperatures and typically see a higher percentage loss.

In work reported by the Electric Power Research Institute (EPRI) in the early 1990s, the relative stability of several amines was listed as:

Monoethanolamine > methoxypropylamine > morpholine

Table 13.5 shows suggested temperature limitations for some of the neutralizing amines commonly used.

Amine	Approximate Temperature Limit, °F (°C)
Ammonia	No limit
Cyclohexylamine	1100 (593°C)
Diethylaminoethanol	850 (454°C)
Morpholine	1100 (593°C)

TABLE 13.5 Recommended Temperature Limitations for Neutralizing Amines

Thermal degradation of the neutralizing amines typically results in the generation of lower molecular weight amines and organic acids, as well as ammonia. For example, the decomposition of morpholine is well known and is shown in Fig. 13.7. The organic acids can cause various problems: cation conductivity is elevated, pH can be depressed in some areas, and condensate polisher (anion) loading is increased. In addition, the original amine is destroyed, and the amines formed are typically more volatile. Thus, the volatility blend provided by the original program is changed, and portions of the condensate system may not be as well protected.

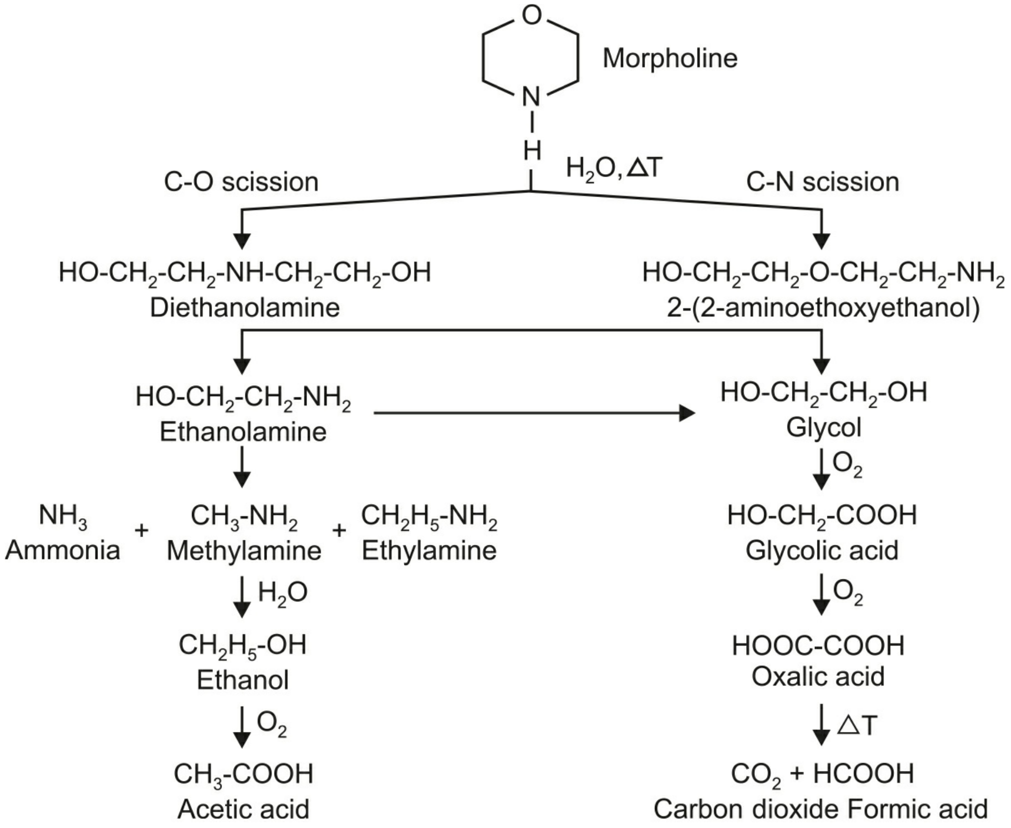

FIGURE 13.7 Decomposition of morpholine.

In high-pressure power plants, the benefits of feeding neutralizing amines must always be weighed against potential problems caused by increased total organic carbon (TOC) and cation conductivity.

Amine Recycle

Much of the neutralizing amine fed to a boiler system is recycled. The total amine present in a boiler system is a combination of the amount of amine returned with the condensate, plus the existing amine feed rate. Feed rates can be reduced substantially by returning higher amounts of condensate.

Losses include:

- Sewered or lost condensate—all amine present is lost with the condensate.
- Vented returns—primarily the more volatile amines (cyclohexylamine). A larger portion of CO_2 is generally lost than amine.

- Condensate polisher—depends on regeneration practices. Condensate polishers are capable of removing neutralizing amines, but many are run past the amine breakpoint. In addition, condensate polishers regenerated in the amine form will not remove amines.
- Deaerator venting—limited due to low mass flow rate and feedwater pH. The pH must be equal to or greater than the amine pKa for appreciable loss to occur.
- Boiler blowdown—depends on amine and blowdown rate. Loss of amines with low *V/L* ratios is greater than those with high *V/L* ratios. Mass loss is greater at low cycles than at higher cycles.

The total amine present in a boiler system is a combination of the amount of amine returned with the condensate (recycled) plus the fresh amine feed rate. Product feed rates can be reduced substantially by returning higher amounts of condensate.

Dosage Requirements

Neutralizing amine programs are generally effective when fed to maintain a condensate pH of 8.5 to 9.2 in systems with soft water makeup or 9.0 to 9.6 in systems with demineralized makeup. In systems containing copper alloys, a range of 8.8 to 9.2 provides optimum corrosion protection for both ferrous and copper alloyed portions of the system. Because the amines are added to the system in direct proportion to the amount of CO_2 in the steam, high-alkalinity feedwater requires considerable amounts of amine to obtain the desired pH range. The cost of such a program may be prohibitive, and alternative means of corrosion protection should be sought. Common pretreatment alternatives of the makeup water that reduce amine dosage requirements include dealkalization, demineralization, and reverse osmosis (RO).

Neutralizing amines themselves offer no protection from oxygen corrosion. Because they do elevate the pH, however, they can provide some indirect inhibition to oxygen attack, if the pH is raised to 9.5 or higher. If air inleakage is a problem in a system, an alternative must be considered. The use of filming materials in combination with neutralizing amines may be the cost-effective alternative needed for high-alkalinity systems or systems plagued by air inleakage.

Government Regulations

There are a great number of government regulations that govern the use of amines in steam. Two of the more commonly regulated areas are food contact and airborne concentrations. The regulations discussed here are for the United States. Different regulations of similar nature may apply in other countries.

In the processing of food, substances contacting the food (including any substance intended for use in producing, manufacturing, packing, processing, preparing, treating, packaging, transporting, or holding food) have the potential to become part of the food. As such, they are regulated by the U.S. Food and Drug Administration (FDA). Boiler water additives used in the generation of steam fall into this category. Under FDA regulations, only certain neutralizing amines can be used in the treatment of steam and condensate systems. In addition, their concentrations must remain below the specified limitations summarized in Table 13.6.

Substances	Limitations
Cyclohexylamine	Not to exceed 10 mg/L in steam, and excluding use of such steam in contact with milk and milk products
Diethylaminoethanol	Not to exceed 15 mg/L in steam, and excluding use of such steam in contact with milk and milk products
Morpholine	Not to exceed 10 mg/L in steam, and excluding use of such steam in contact with milk and milk products
Octadecylamine	Not to exceed 3 mg/L in steam, and excluding use of such steam in contact with milk and milk products
The combined total of all amine concentrations must remain below 25 mg/L total actives.	

Source: 21 CFR 173.310(d) Boiler Water Additives.

TABLE 13.6 U.S. FDA Regulations for Amines

Boiler water additives used in the generation of steam for federally inspected meat or poultry, shell egg grading, or rabbit and egg processing facilities had historically been governed by the U.S. Department of Agriculture (USDA). In 2000, the National Sanitation Foundation (NSF) assumed previous USDA evaluation and registration responsibilities in this area. Approval by

NSF should be listed on any product's Safety Data Sheet (SDS). USDA/NSF approval is by product and not by product component.

Often, steam from boilers is used to humidify building air, especially during the winter. When steam is introduced into the air, any volatile compounds contained in the steam are also introduced into the air. The American Conference of Governmental Industrial Hygienists (ACGIH) and the U.S. Occupational Safety and Health Administration (OSHA) are the two regulating bodies for airborne substances in the United States.

ACGIH has adopted standard threshold limit values—time weighted averages (TLV-TWA) for amines in air, based on their irritative properties. The TLV-TWA is the time-weighted average concentration to which nearly all workers may be exposed for eight hours per day, forty hours per week, without adverse effect. OSHA has established time-weighted average permissible exposure limits (PEL) for commonly used amines. These limits and odor threshold values are listed in Table 13.7. To date, no major agency or association has prohibited the use of steam treated with chemical additives for humidification, but questions and concerns about such use are common.

Amine	ACGIH TLV-TWA mg/L	OSHA PEL-TWA mg/L	Odor Threshold mg/L
Morpholine	20	20	0.14
Diethylaminoethanol	2	10	0.04
Cyclohexylamine	10	10	0.90

TABLE 13.7 Neutralizing Amine TLV, PEL, and Odor Threshold Summary

Filming Amines

Filming amines are high molecular weight amines consisting of very long-chain hydrocarbons. One end of the molecule is hydrophilic (attracts water), and the other is hydrophobic (repels water). The hydrophilic end physically attaches itself to the metal surfaces of the condensate system. As the density of the molecules on the metal surfaces increases, the hydrophilic ends create a monomolecular, nonwettable film on all metal surfaces that come in contact with the condensate. This film acts as a physical barrier between the metal surfaces and corrosive condensate, offering protection against both carbon dioxide and oxygen attack (Fig. 13.8).

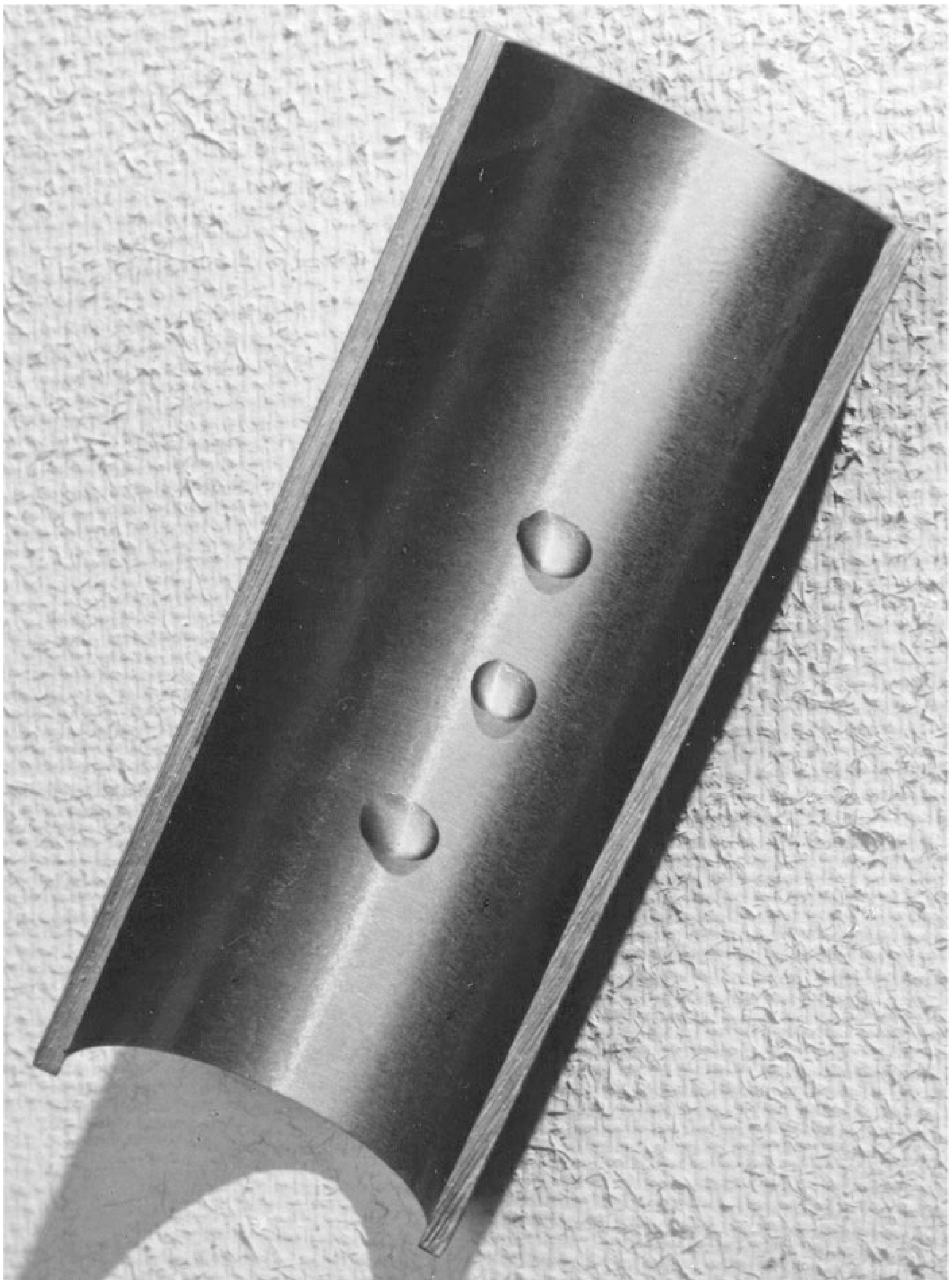

FIGURE 13.8 Condensate pipe treated with filming amine repels water.

Unlike neutralizing programs, filming amine programs do not neutralize CO_2. Therefore, their feed rates are not directly proportional to the amount of contaminant (O_2, CO_2, NH_3, etc.) in the steam. The amount of filming amine required is related to the system's surface area. This fact makes a filming amine program desirable in systems with high-alkalinity feedwaters or in areas of air inleakage, where a neutralizing program would be either cost-prohibitive or ineffective.

The protective amine film is generally quite stable, but high pH conditions may cause it to strip off the metal (pH above 8.0 for octadecylamine), while low pH (below 6.5) impairs the film adsorption on metal. Supplemental neutralizing amines or combination neutralizer/filmer programs are often necessary to maintain the correct pH control range. Filming amines can be worn or eroded away by the flow of water across the metal surface. They must be fed continuously to assure that no gaps in protection occur in any parts of the system.

Caution must be exercised when a filming amine program is started. Filming amines tend to clean up any iron oxide, scale, or contaminant on the piping while attaching to the metal. This may initially result in higher levels of solids in the condensate. In addition, excessive feed may cause the filming amine to accumulate as sticky masses (gunk balls) in receivers, steam traps, valves, or any collection point. Periodic testing is required to maintain a specified residual of filmer in the condensate to avoid such deposits. A filming amine program should start with a low dosage, which is gradually increased until residual limits are met.

Oxygen Scavengers/Metal Passivators

Volatile oxygen scavengers can be used in combination with neutralizing amines. The scavenger reacts directly with oxygen present in the condensate, while the neutralizing amine provides protection from CO_2 corrosion. Volatile oxygen scavengers may also enhance or accelerate metal passivation, but their ability to do this varies greatly. At condensate temperatures, metal passivation may preferentially occur over oxygen scavenging. Oxygen corrosion inhibitors do not provide protection against carbon dioxide or ammonia. Carbonic acid attacks the passive magnetite film, so passivation improves greatly above pH 8.3, where this acid is not present. Most of these chemicals are a potential source of ammonia.

Sulfite is not acceptable in condensate systems, because it adds solids to the condensate and is not volatile. Erythorbate is not volatile but can be used in condensate systems, if fed into the condensate. It should not be fed directly to the steam. Hydrazine, carbohydrazide, and diethylhydroxylamine are oxygen corrosion inhibitors that can be fed directly to the steam. Carbohydrazide reacts with oxygen both directly and through the generation of hydrazine. A pH of 8.5 must be maintained to promote a passive metal surface. Filming amines are usually more cost-effective than oxygen corrosion inhibitors.

Minimizing the Effect of Contaminated Condensate

Steam condensate is usually recycled because the condensate is a valuable product and its reuse is considered essential to the economics of steam and power production. Although impurities in condensate are usually quite low, in some instances they must be removed before the condensate can be reused, or the condensate must be discarded. These impurities originate from dissolved solids introduced through condenser leaks, dissolved solids carried over with the steam from the boiler water, metallic species originating from condensate equipment corrosion, and various process contamination events.

Condensate polishers can be used to improve the purity of condensate. The primary purpose of condensate polishers is to filter corrosion products such as iron and copper oxides (crud). They also remove traces of soluble salts, resulting from condenser leakage and carryover.

Another means of minimizing the effect of contaminated condensate is to discard it before it reaches the polishers. Depending on the degree of contamination, this is often a prudent action. Badly contaminated condensate may quickly exhaust or foul polishers, allowing the full amount of contamination to return to the feedwater system.

Automatic diversion systems can be used to detect and discard condensate that is unfit for reuse. These systems must be installed properly to be effective. Velocities of pumped condensate returns are commonly 6 to 8 ft/s (1.8–2.4 m/s). Automatic control valves can take 4 to 5 seconds to actuate, close, and divert the condensate to sewer. This means there must be a minimum of 24 to 40 ft (7.3–12 m) between the detection device and the valve, if all contamination is to be prevented.

Most detection devices require additional response time, since they often need a cooled sample and are not located immediately on the return condensate line. Sample line size (diameter and wall thickness), length, and volume determine how much additional response time this adds. Additional time is required for the contaminant to rise to the alarm concentration. There may also be a lag time inherent in the method of analysis or detection device that must be added to the total response time. Each of these factors increases the distance required between the detection device (or sample tap) and the automatic dump valve.

The required distance quickly becomes excessive, and a failure of either the valve or the detection device allows contamination back into the boiler system. Industrial plants with potentially troublesome condensate have learned that it is much more reliable to install a redundant automatic diversion system than to rely on a single system and try to get sufficient distance between the sample tap and valve. The first automatic diversion valve and detector should be close to the point of potential contamination. The second system can be just before the final condensate collection tank and monitor combined return streams. Be sure to consider the amount of condensate dumping that can be tolerated. This is generally considered to be the amount of extra makeup that the pretreatment can supply.

If the contaminant is cationic or anionic in nature, it may be detectable by simply monitoring specific or cation conductivity. Many particulates, suspended solids, and organics are nonionic, however, and do not affect conductivity values. In those plants, an in-line TOC monitor may be used to detect organic condensate contamination. Turbidimeters, particle counters, fluorometers, and chromatographs have had some success in detecting certain nonionic organic contamination. Turbidimeters and particle counters are most commonly used to detect particulates or suspended solids such as particulate iron.

Valves should be exercised and meters calibrated to assure they are working properly. Meter measurements should be verified by grab sample at a frequency that assures the protection and reliability of the boiler system. The required frequency depends on the reliability of the meter, frequency of condensate contamination, and the effect of the contaminant on the boiler system, but should typically be done at least once per week.

System Design and Maintenance

Steam condensate system design and maintenance not only affect the delivery of steam, but also the ability to remove condensate from the system and the potential for system corrosion. Poor drainage of condensate can result in corrosion, erosion, and water hammer, all of which eventually result in leaks and failures and limit the amount of condensate returned for reuse as boiler feedwater.

It is not within the scope of this chapter to thoroughly discuss all the design issues that might affect a plant’s ability to return condensate. However, common good engineering practices are listed below:

- Supply dry, high-quality steam. Steam quality must generally match process requirements and be of sufficient quality (dryness) not to erode system components. In those instances when high-moisture steam is used, a steam separator should be considered. Supply lines should be insulated and trapped to prevent accumulation of condensate.
- Isolate steam from unused lines with properly located isolation valves. Any dead leg open to steam should be trapped to prevent condensate accumulation.
- Make sure lines and traps are properly sized. This minimizes pressure loss, erosion, heat loss, and blow-through steam. Horizontal lines should be sloped at 1 inch per 10 feet (8.3 mm/m) in the direction of flow and properly supported to prevent sagging and condensate accumulation.
- Install sufficient traps on steam mains to remove condensate as quickly as possible. At a minimum, traps should be located on all vertical risers, upstream of control valves, and at 100 to 300 ft (30–91 m) intervals along horizontal runs of pipe.
- Use the correct trap for the application. Never group trap (using one trap on multiple lines). Group trapping invariably leads to back-up of condensate in the system.
- Ensure that piping allows the condensate to be removed effectively. Coils should be fitted with vacuum breakers to allow condensate to drain freely. Waterlogged equipment not only fails to operate as expected, but is also prone to corrosion and water hammer.
- When possible, avoid any increase in elevation on return condensate lines. Condensate that is evacuated to a higher elevation does not flow by gravity. It requires a pressure slightly greater than the head pressure resulting from the elevation rise. When elevation of condensate after a trap is necessary, a pumping trap may be necessary to assure good drainage.

- Install receiver vents of the proper size. Receiver vent lines that are too small restrict the loss of flash steam. This in turn results in hotter condensate return temperatures and potential problems with cavitation of electric condensate return pumps. Alternatively, use pressure-powered pumps.
- Make sure condensate return lines are sized to move the flash and blow-through steam present after a trap, as well as the condensate. Steam (vapor) is more voluminous than condensate (liquid). Condensate piping that is sized for only liquid is grossly undersized.
- Choose materials of construction that minimize corrosion.
- Inspect and repair steam traps. Steam traps can be a source of significant energy loss (steam and condensate). Implement routine steam trap maintenance programs for regular inspection, testing, and repair of failed traps. In most systems, there is opportunity for significant savings and near immediate payback on the minimal investment required to inspect and repair steam traps.

Evaluating Results

Effective monitoring and control of the steam condensate system is necessary to assure proper corrosion protection. Contamination originating in the condensate system can easily affect the entire boiler system. Without adequate monitoring and control, the system will most likely suffer increased operational costs and unscheduled outages.

The American Society of Mechanical Engineers (ASME) provides excellent recommendations for sampling from boiler systems in their document "Consensus on Operating Practices for the Sampling and Monitoring of Feedwater and Boiler Water Chemistry in Modern Industrial Boilers" (CRTD-Volume 81). The American Society for Testing and Materials (ASTM) has also written numerous documents that cover the practice of sampling boiler system streams.

Successful monitoring and control requires that representative samples be obtained at multiple locations throughout the system. Typically, samples that exceed 100°F (38°C) must be cooled before collection to maintain a representative sample and assure the safety of personnel. Temperature should ideally be maintained at 70 to 90°F (21–32°C), with 77°F (25°C) preferred, to prevent significant loss of volatile gases such as CO_2 and O_2. The sample may be throttled at the outlet but not at the inlet. This is done to prevent a vacuum from occurring in the coil and drawing in air, which can yield false results.

Samples must be taken from a location that is representative of the system. Dead legs or end-of-the-line locations may be convenient, but are seldom representative. If chemicals are injected or other streams introduced into the line to be sampled, the collection point must be placed far enough downstream to ensure a mixed sample. With turbulent flow (Reynolds number > 4000), a tap location 25 pipe diameters downstream is considered acceptable. With laminar flow, a length equivalent to 50 pipe diameters is recommended (ASTM D 3370-95a).

The contaminant typically present in condensate is particulate iron. Particulate iron is not conductive and will not be detected by a conductivity probe. As a particulate, it tends to drop out of the bulk water behind fittings and valves, within wide spots in the line, or wherever velocity is insufficient to keep the particle entrained in the liquid. A long vertical rise typically causes a problem with maintaining particulate iron in the sample (gravity works against the particle remaining in the bulk water).

Why Treat Condensate?

The industry practice of treating condensate exists because it is usually more cost-effective to treat condensate than to live with the results of corrosion. Even plants that do not return any condensate can save many of the costs listed below through condensate treatment.

Condensate corrosion results in many additional plant costs:

- Increased fuel consumption due to steam and condensate leaks throughout the steam and condensate systems
- Replacement costs for equipment, heat exchangers, lines, tanks, steam traps, etc.
- Increased maintenance costs
- Unscheduled outages and loss of equipment use that lead to

production losses

- Equipment fouling, which can affect product quality if design conditions cannot be maintained
- Dirty condensate
  - Can result in dirty boilers, increased fuel consumption, reduced boiler reliability, and boiler failures
  - May require sewering because it is unfit for reuse as boiler feedwater
  - May require clean up (e.g., filtration or polishing), incurring additional costs for reuse

SECTION 3.3

Applications—Cooling Water System

CHAPTER 14

Cooling System Dynamics

Mechanical-Operational-Chemical Survey Concepts

A complete mechanical-operational-chemical (MOC) survey provides mechanical details about the process and cooling system, collects operating history data, evaluates costs of operation, and details the chemistry of the system. Every cooling water system presents a unique combination of equipment, operating controls and history, water chemistry, and contaminants. The goal of the survey is to understand the interactions between the mechanical, operational, and chemical aspects of the entire system.

Data collected in the survey should be compared to design specifications to evaluate current operation versus initial design. Differences can help point to opportunities for improvements, areas of stress in the system, or problems that need to be solved. System stress can be defined as any mechanical, operational, or chemical factor that negatively impacts system performance. Examples of system stress include high surface temperature in heat exchangers, low flow rate, high concentration ratio, or poor control of tower operating parameters. Exceeding any of these stress points can cause corrosion or fouling of the system. Responses to reduce or control system stress include adjustments to the chemical treatment program, concentration ratio adjustment, or mechanical improvements to the system. Optimizing the treatment program for the system stress points will provide the optimum results and the best value for that system. The chapter on cooling water treatment (Chap. 19) will cover cooling water system stress and the proper responses to different stresses in more detail.

Survey Data Analysis

Analysis of the information collected can identify stresses in a cooling system, like scale in a high-temperature, low-flow heat exchanger or corrosion problems due to control parameter variability. These stresses on a cooling system are very system specific. Using these data, a program can be designed to manage the system at the optimum points for stress and lowest cost. The goal is to be able to maintain a reasonable level of stress in the system at the lowest operating cost. Assessment of the impact of various stresses involves understanding the costs of different treatment program operating modes. Consequently, to be able to demonstrate the value of stress management, identification of the stresses with greatest impact on cooling water system performance is essential.

Modeling the water chemistry under different conditions is a valuable method to determine the scaling potential of the system. Computer modeling programs can evaluate potential mineral scale formation, corrosion tendencies, and treatment programs under a wide range of cooling water system conditions. Computer modeling programs can be used for thorough analysis of stresses due to water chemistry and control variability. These programs can quickly indicate conditions that may cause problems at various concentration ratios, pH, or contaminant levels. This can show the correct operating conditions to optimize system operation at optimum stress levels. The impact of poor control is poor results, and each control parameter may have a different effect on the system (Fig. 14.1). Often, system control is the most important element for successful operation of a cooling water system.

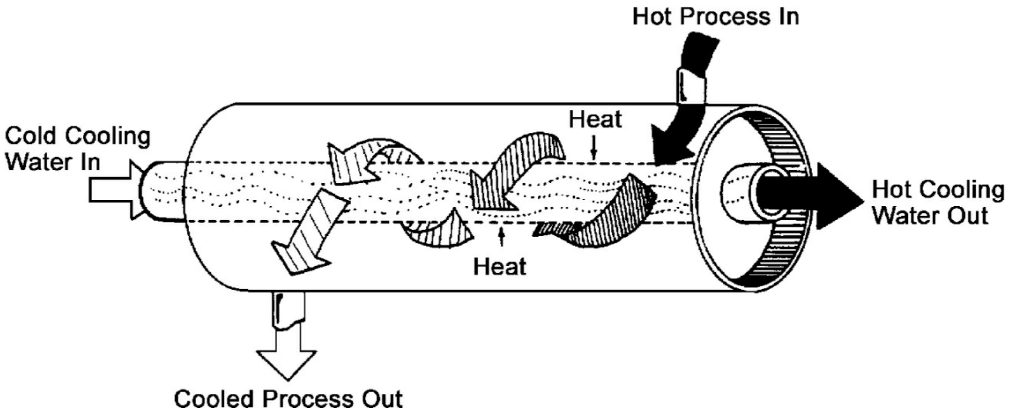

FIGURE 14.1 Heat flows from the hot process to the colder cooling water in this simple example of a heat exchanger.

The next step is to understand the extent to which these key stresses affect the total cost of operation (TCO) as shown in Fig. 14.2. By understanding the total costs of the cooling water system operation and treatment, the best return on investment (ROI), and best environmental return on investment (e^{ROI}) can be achieved. The MOC concepts provide a complete framework to gather and analyze the information needed to reach the optimum TCO and the best ROI from an optimized program. This chapter illustrates the key parts of an MOC survey: heat transfer and heat exchangers, cooling water system types, and system dynamics calculations.

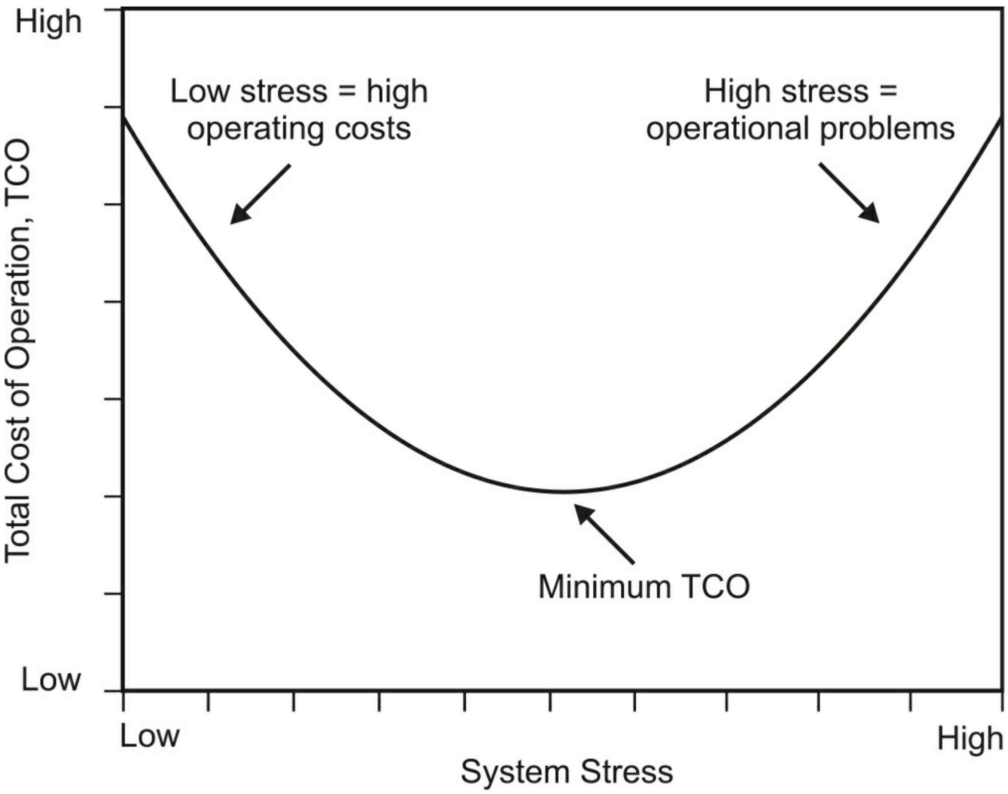

FIGURE 14.2 Optimum TCO is a balance between stresses that are too high and too low.

Heat Transfer

Heat transfer is the science that deals with the exchange of heat between hot and cold bodies. By definition, heat passes from the warmer medium to the cooler one. In typical industrial applications, the product or process being cooled is the heat source and cooling water is the receiver. Cooling water usually does not contact the heat source directly. The process fluid or gas to be cooled is usually separated from the cooling water by a barrier that is a good conductor of heat, usually a metal. The barrier that allows heat to pass from the source to the receiver is called the heat transfer surface, and the assembly of barriers in a containment vessel is a heat exchanger. A heat exchanger is a device for transferring thermal energy from one medium to another, as for example, between two liquids or between a gas and a liquid. Generally, an exchanger consists of two sections, one for each medium.

There are three distinct ways in which heat may pass from a source to a receiver, although most engineering applications are combinations of two of the methods. These are conduction, convection, and radiation. Conduction is how metal transfers heat from one part of the metal to another part. The metal components of the heat exchanger carry heat away from the process fluid by conduction. Convection is primarily how fluids (liquids and gases) transfer heat within the fluid itself. Rapid water flow is very important in heat exchangers, because water turbulence assists the convection process in distributing the heat throughout the water. Finally, radiation is the transfer of heat in the form of energy rays or waves, like infrared energy. Light from the sun heats the earth by radiation. Similarly, the return water piping of a cooling system will lose some heat by radiation to the surrounding atmosphere.

Figure 14.3 illustrates the three methods of heat transfer with a burning candle. The hot gases from the flame carry heat into the air by convection. The convection currents in the air can be seen by the distortion of view when looking through the air above the candle. Heat radiation is felt by placing a hand near the side of the flame. The hot wax under the flame carries the heat into the candle by conduction through the wax.

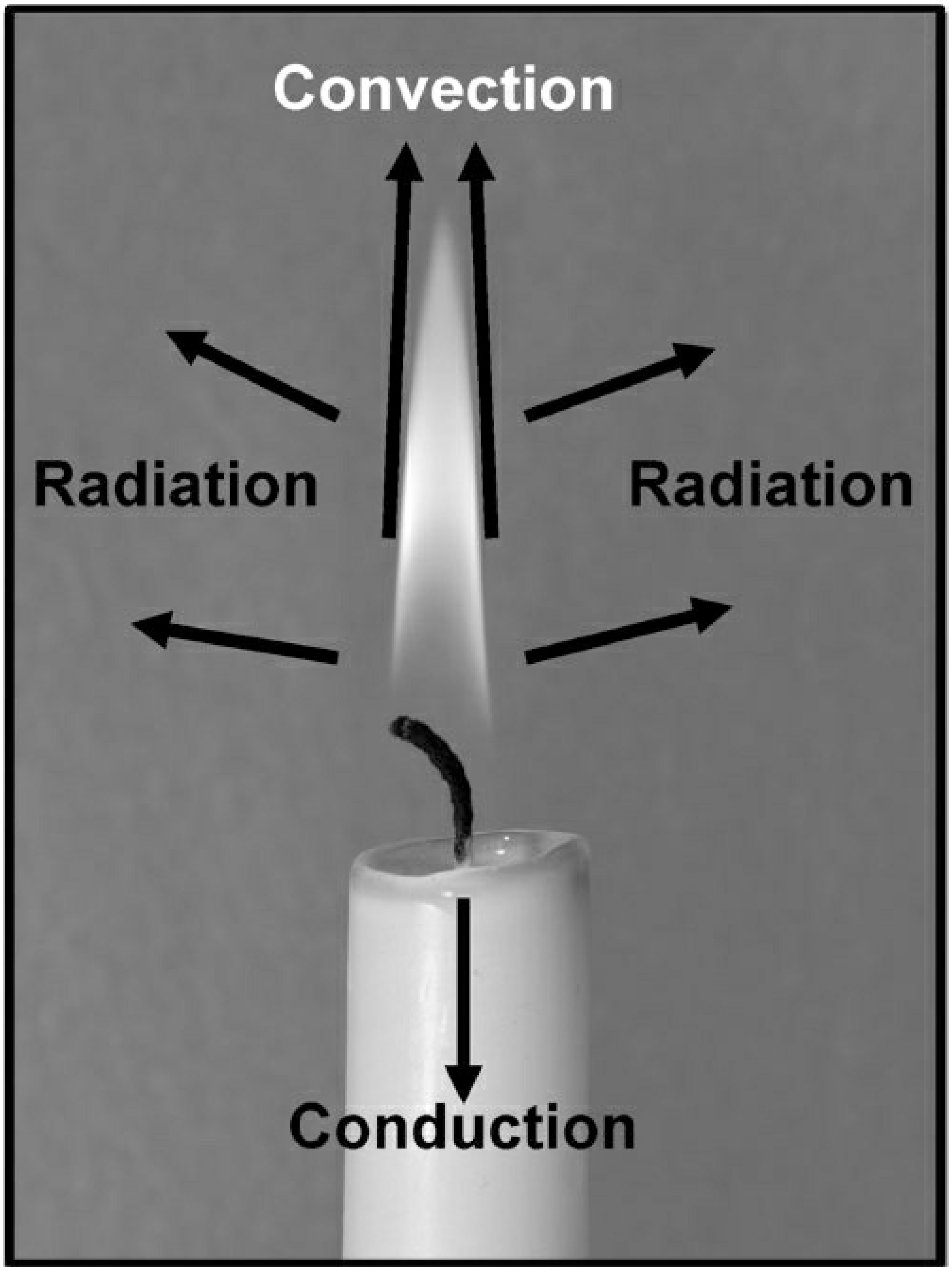

FIGURE 14.3 Illustration of the three processes of heat transfer.

Heat Exchangers

The most common of all heat exchangers is known as the shell-and-tube exchanger. In this exchanger, one medium flows through a bundle of tubes, while the second medium passes around this bundle inside the exchanger shell, as shown in Fig. 14.4. No matter what the configuration, the exchanger must be arranged so that the maximum amount of surface exists between the fluids exchanging heat. This can be achieved by running one fluid back and forth in two or more "passes" on the tube side (the water makes two passes in the exchanger in Fig. 14.4), while the other fluid flows across the outside of the tubes around baffles on the shell side.

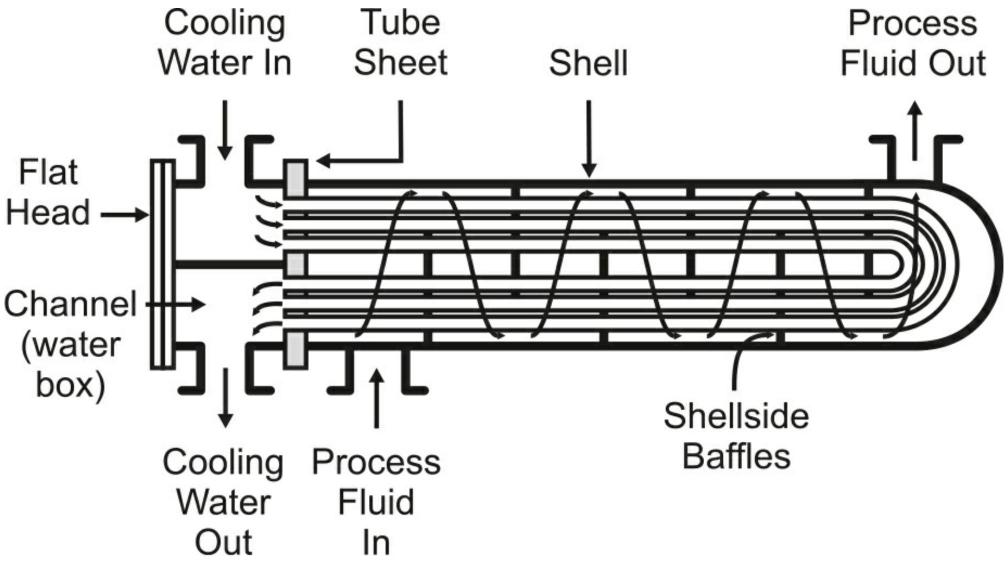

FIGURE 14.4 Assembly of a simple two-pass heat exchanger with water on the tube side and a U-tube bundle.

Heat exchangers fulfill a variety of generic heat transfer functions. Some functions include a change of state of either the process fluid or the coolant (or both), while others do not. These are a few of the important considerations made when determining the value contributed to a process by the cooling water:

- Exchangers condensing process liquids are the highest value exchangers in a chemical plant or refinery. Problems with condensing exchangers result in loss of production or environmental violations. If a leak violates environmental laws, immediate shutdown will incur excessive costs. Overhead condensers may provide a subcooled liquid for a separation tower reflux, which then requires additional heating. A hot reflux may result in off-specification product or causes reduced production in a separation tower.
- Surface condensers allow turbines to develop maximum vacuum. Loss of vacuum on the condensing side due to water-side fouling or scaling

of the condenser will limit production or increase utility costs.

- Refrigeration condensers are found in all businesses. In the institutional market, the cost and maximum refrigeration capability are affected by condenser performance. In industrial plants, poor performance will have similar effects but are typically not recognized because the refrigeration systems are low priority. Ethylene plants use propylene as the working fluid, and refrigeration may limit production in the warmer months. The topic of refrigeration and chillers is covered in Chap. 39.
- Run-down coolers cool a stream leaving a unit going to storage. Normally, run-down coolers are low-value exchangers. The exception is when a stream is not sufficiently cooled and vent losses occur from the storage vessel.

No matter what type of exchanger is used, six factors will affect heat transfer in an exchanger:

1. Heat transfer characteristics of the metal—its thermal conductivity
2. Thickness of the metal
3. Heat transfer surface area
4. Velocity and turbulence of both the process stream and cooling water
5. Temperature difference between the process stream and the cooling water
6. Deposits of any kind on either side of the heat transfer surface

The first four of these are inherent in the design of the exchanger, while the last two are operational characteristics that change depending on the conditions of service. Deposits on either side of the barrier have lower thermal conductivity and reduce the efficiency of the heat exchanger (Fig. 14.5). This reduction of heat transfer efficiency means that the cooling water may not remove sufficient heat from the process. Therefore, production must be slowed or the flow of cooling water must be increased to maintain the same cooling rate available before fouling developed. Frequently, the latter is not possible, and the productivity of the process unit or the entire plant is reduced.

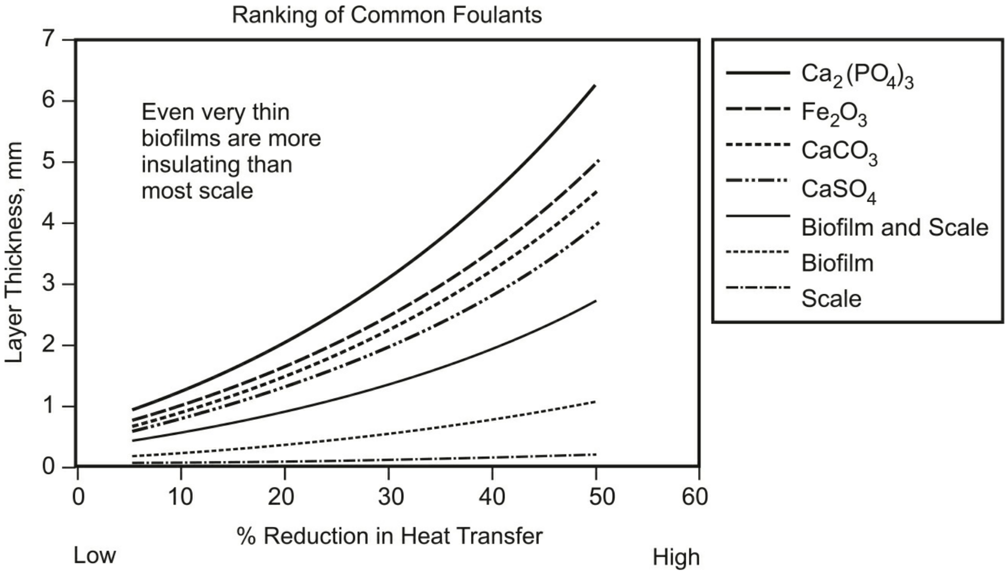

FIGURE 14.5 Insulating power of common foulants in heat exchangers.

Shell-and-Tube Heat Exchanger

Shell-and-tube heat exchangers come in a variety of shapes, sizes, and designs. Exchangers are typically classified by physical characteristics, such as the side in which the water flows (on the shell side or tube side), the number of passes on the tube side, the type of head (fixed or floating), or the type of bundle (U-tube or straight through).

Cooling water can be on either the tube side (inside the tubes) or shell side (surrounding the tubes) of an exchanger. From a water treatment perspective, there are significant advantages to having tube-side water. With this type of exchanger, water velocity is usually maintained above 2 to 3 ft/s (0.6–0.9 m/s) to as high as 7 to 8 ft/s (2.1–2.4 m/s), to help keep the tube walls free of suspended solids deposition. Lower water velocity encourages deposition of suspended solids in the tubes (Fig. 14.6). In a bundle of tubes, perhaps only one tube may have a low velocity due to plugging or poor distribution. Occasionally, high pressure on the process side can be handled more economically with cooling water on the shell side of the exchanger. One major problem in such exchangers is the low flow velocity frequently encountered around baffles, tube supports, and tube sheets, even when the average flow velocity through the shell appears acceptable. These low velocity areas influence skin temperature and greatly increase the potential for deposits and rapid metal deterioration. For example, critical mild steel exchangers with water on the shell side have been known to fail from perforations in as little as three months due to excessive deposition, even in the presence of a strong corrosion inhibitor.

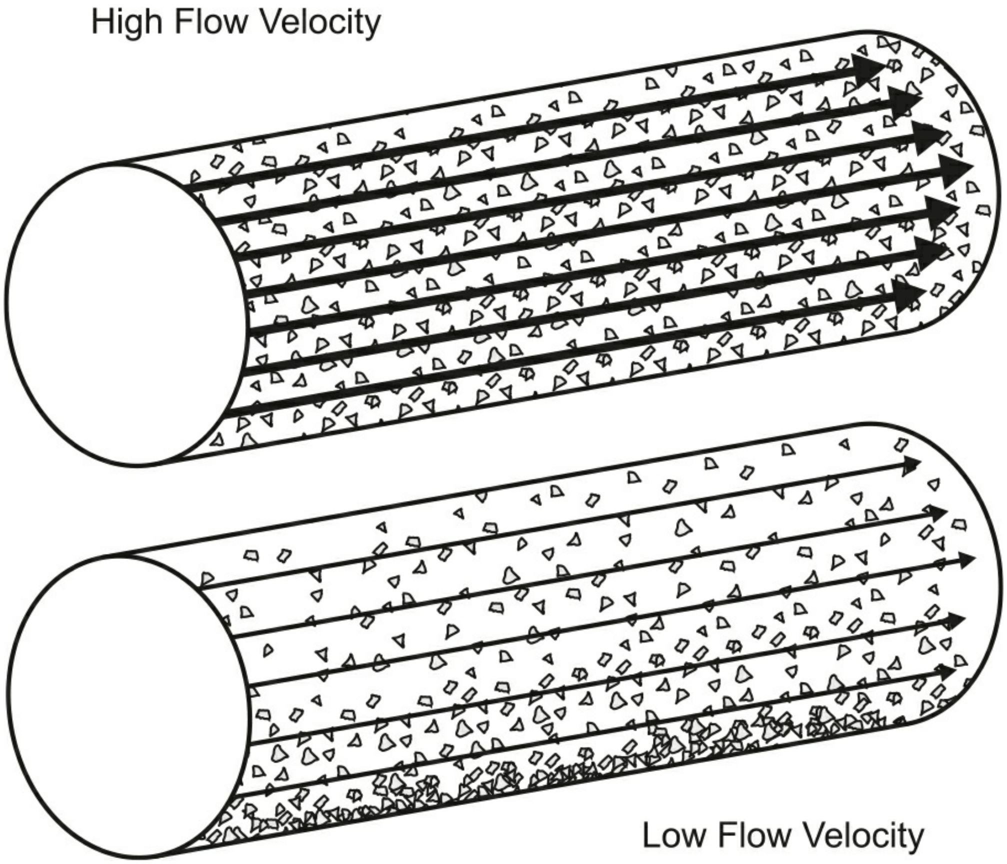

FIGURE 14.6 High flow velocity can help to keep insoluble particles suspended in the water, but low flow velocity will allow particles to settle onto the bottom of the tube surface.

Surface Condensers

Surface condensers are a special type of shell-and-tube exchanger found in electric utility operations and often in industrial plants, where a process fluid must be condensed. In the utility application, the primary function of a surface condenser is to reduce the turbine exhaust steam pressure and temperature to the lowest possible levels, thereby providing greatest turbine efficiency. A second function of surface condensers is to recover condensate and a small part of the exhaust steam heat. See Chap. 33 on the Power Industry for more details on surface condensers in utility applications.

Plate-and-Frame Heat Exchanger

These exchangers are constructed of a series of plates held in a frame and separated by gaskets and corrugations in the plates (Fig. 14.7). The total number of plates and the manufacturers stated area per plate determines the area of the exchanger. Plate-and-frame exchangers are a space-saving design, because these exchangers are typically much more compact than a shell-and-tube exchanger of the same surface area. Stainless steel and other corrosion resistant alloys can be used more economically because of the smaller size. However, fouling problems can be more severe because of the small flow passages for water between the plates. This can result in under-deposit corrosion or microbiologically influenced corrosion (MIC).

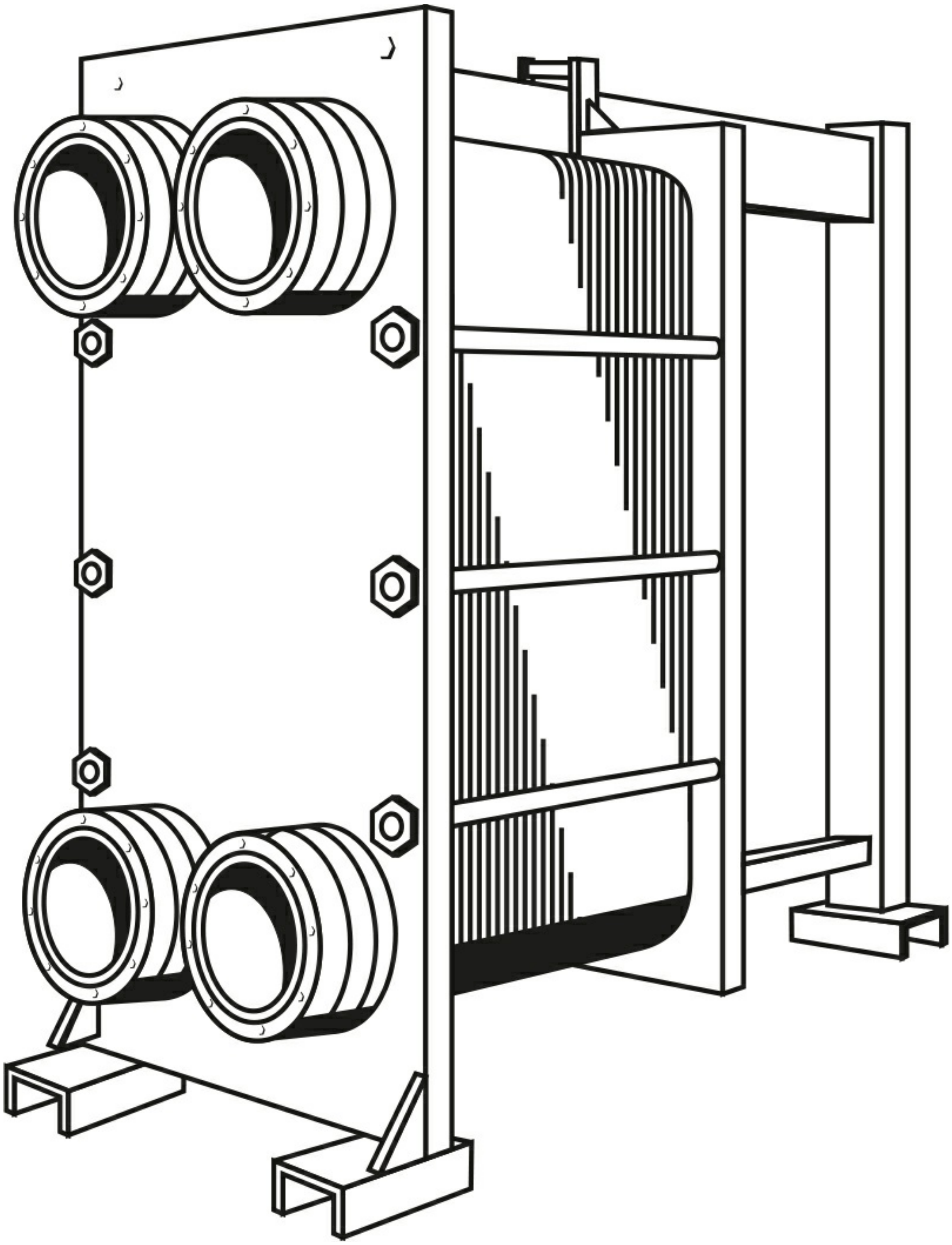

FIGURE 14.7 An assembled plate-and-frame heat exchanger.

Spiral Flow Heat Exchanger

These exchangers are formed from either tubes rolled in a spiral or plates formed in a spiral. The exchanger formed by tubes is placed inside a shell through which the other fluid passes. The spiral plates allow the process to flow on one side of the plate and the cooling water to flow on the other side of the plate. End plates with gaskets prevent mixing of one fluid into the other.

These types of exchangers are not common but have applications in condensate cooling and recovery and in cooling viscous fluids and slurries.

Reactor Jacket Cooling

Reactors, mix tanks, blend tanks, and other reaction vessels are often surrounded by jackets or coils that can heat or cool the vessel contents during processing. The jacket around the vessel, sometimes called an annular space heat exchanger, is typically an open space surrounding the vessel through which steam, cooling water, brine, or a combination of these fluids can flow. A number of jacket designs can be found in common use. Jackets can be plates welded around the outside of the vessel to form one compartment or multiple compartments segregated by baffles. Jackets can also be formed by welding half-pipe sections onto the outside of the vessel in a spiral pattern. Some reactor jackets have a dimpled appearance and are called a dimpled plate jacket.

Design and common usage of reactor jacket systems creates significant challenges for proper treatment and control of corrosion and deposition. The reaction vessel is often coated or constructed of a special alloy to resist corrosion. The jacket, however, is usually constructed of mild steel. This creates the potential for galvanic corrosion, where the steel jacket contacts the alloy of the reactor vessel walls. Low flow rates, irregular flow patterns, and restricted areas are common in the jacket space. Areas of low water flow may result in boiling or alternately wet and dry conditions that can result in severe water-side problems. In many cases, steam is used for heating to initiate reactions, and then cooling water is required to remove heat as the reaction progresses. Treatment of annular space heat exchangers is difficult under the best conditions, but treatment can be further complicated by the alternating use of steam and cooling water to heat and cool a reaction vessel.

Continuous Caster Mold

Continuous casting is the process in which molten steel is continuously poured into a mold that gradually solidifies the steel so that the formed steel shape is extruded out the bottom of the mold onto a work platform. The continuous caster mold is a unique heat exchanger, because of the exceptionally high amount of heat being transferred across a relatively small mold surface. Heat flux is often more than 1 million Btu/[h · ft^2] (3150 kW/m^2) and results in water-side skin temperatures of 250 to 300°F (120–150°C). This extremely high skin temperature is a strong driving force for scale formation. Scale deposits only a few mils (25.4 µm/mil) thick on the water side of the mold can result in serious problems, such as a poor quality cast, or worst of all, breakout of molten steel through the mold wall.

Special Tube Applications

Some heat exchangers contain special tubes to improve heat transfer efficiency. These are generally used in special applications, and the tube enhancement may be on the process side or the water side of the exchanger. Excessive deposition and under-deposit corrosion may occur on the tube surface, depending on the type of tube and whether the cooling water contacts the fins or grooves on the tubes. Examples of some of these tube enhancements are shown as follows.

Raised Fin Tube Heat Exchangers This modification provides increased external surface area by means of fins on the outside of the tube. The fins may appear as discs, helical fins like screw threads, or longitudinal fins (Fig. 14.8). The fins may be either welded or peened to the surface of the tube. Air handlers, radiators, and fin-fan coolers are examples of exchangers using raised fins.

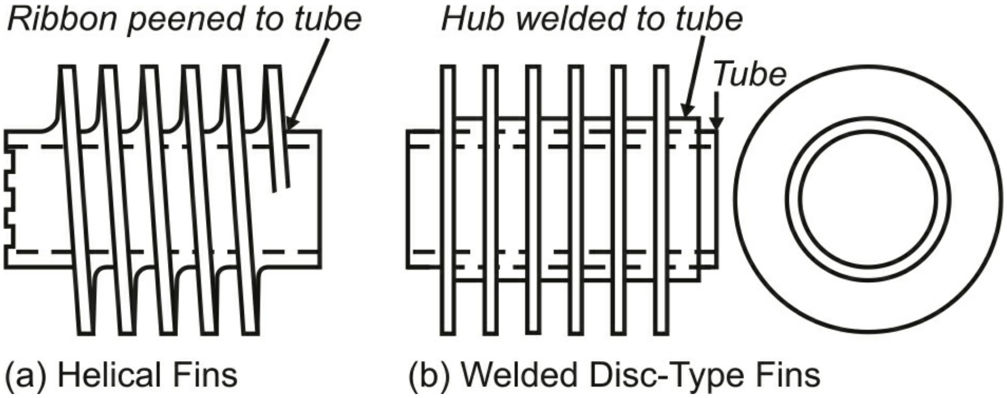

FIGURE 14.8 Examples of tubes with raised fins.

Integral Low Fin A tube commonly found in refrigerant condensers and hydrocarbon process plants is called an integral low-fin tube (Fig. 14.9). A standard tube is formed with small fins on the outside of the tube such that the outside diameter conforms to a standard tube dimension. The ends of the tube are left bare where the tube passes through the tube sheet.

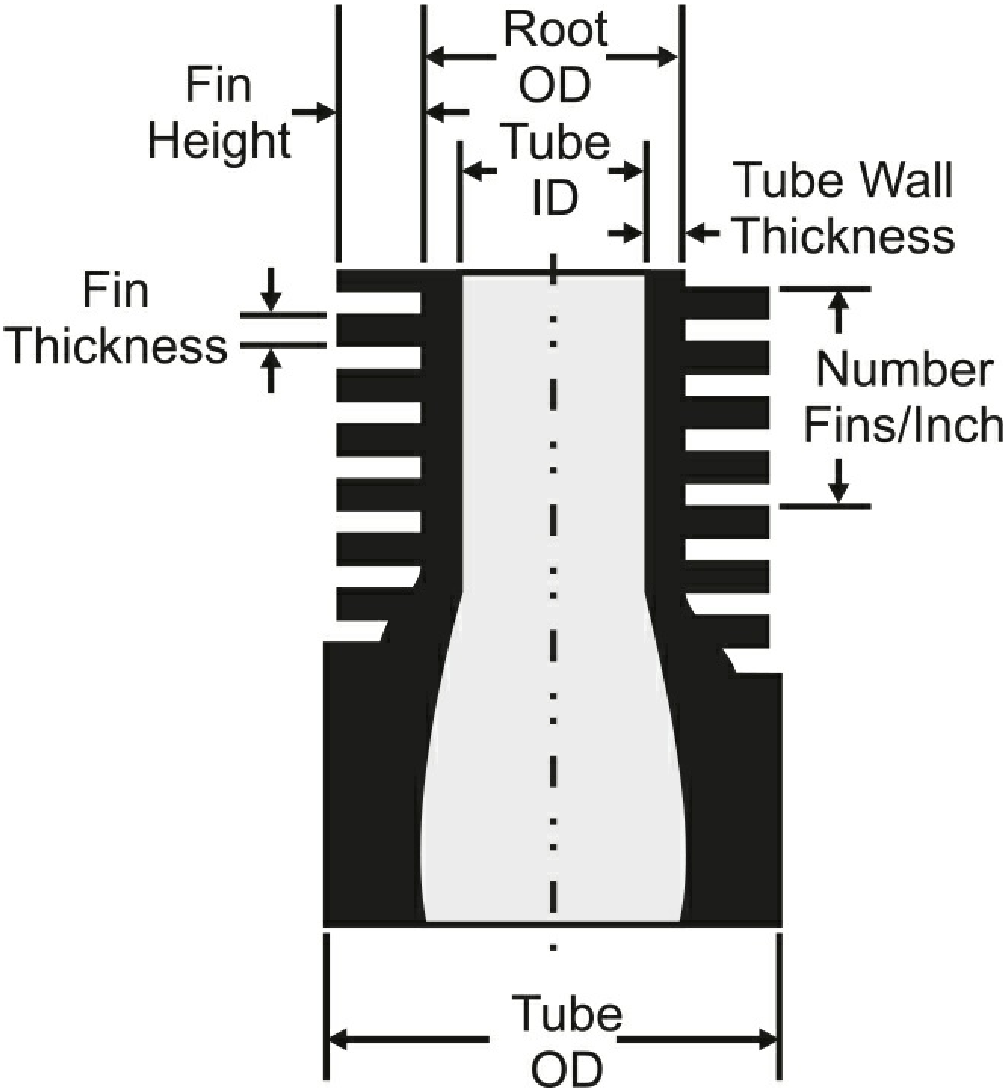

FIGURE 14.9 Example of an integral low-fin tube.

Rifled Tubes Rifled tubes are used in some refrigeration equipment where either chilled water or condenser water flows through the tube. “Rifling” refers to cutting spiral grooves along the length of the inside of the tube. Theoretically, rifling increases turbulence and subsequently the heat transfer coefficient. The equipment manufacturer can provide a smaller evaporator or condenser due to the increase in the heat transfer coefficient. The grooves in the tube must be kept very clean to achieve the desired effect on heat transfer. Fouling of the grooves will decrease heat transfer and lead to severe under-deposit corrosion. Cleaning of the tubes is difficult, and the grooves must remain sharp and clean to produce the increase in heat transfer. Figure 14.10 shows an example of a rifled tube with deposition covering localized corrosion sites in the grooves.

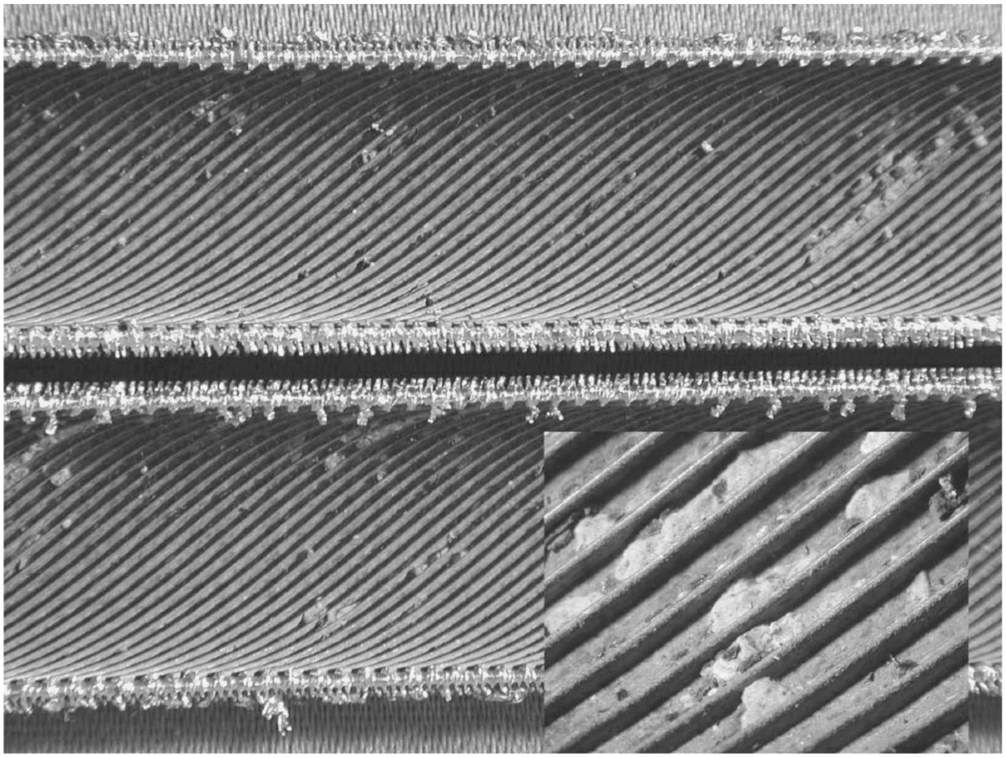

FIGURE 14.10 Rifled condenser tube removed from a refrigeration chiller and split longitudinally. The deposits are the result of localized corrosion in the grooves. The inset image shows an enlargement of part of the tube to illustrate how the deposit over the corrosion sites can fill the grooves.

Calculations and Measurements

Performance monitoring of heat exchangers is essential to understand the operation of a system and obtain best results from any treatment program. Several design parameters should be calculated and compared to the original system design to determine if changes have occurred. Many of the measurements and calculated performance values should be determined over a period of time and evaluated with trend analysis tools. Examples of some of the more common parameters and how these calculations can be used will be described.

Approach Temperature

This value is easy to determine if water and process temperatures are measured for an exchanger. Approach temperature can be used as a first step in monitoring performance of exchangers where condensation does not occur or in process condensers where the condensate is not cooled below the condensation temperature (no subcooling of the condensate). The simplest definition of approach temperature is the difference between the process outlet temperature and the cooling water inlet temperature (Fig. 14.11). The closer these two temperatures approach each other, the greater the cooling efficiency of the exchanger. Approach temperature is sensitive to changes in both water and process flow, and temperature, and is only a rough indicator of exchanger performance.

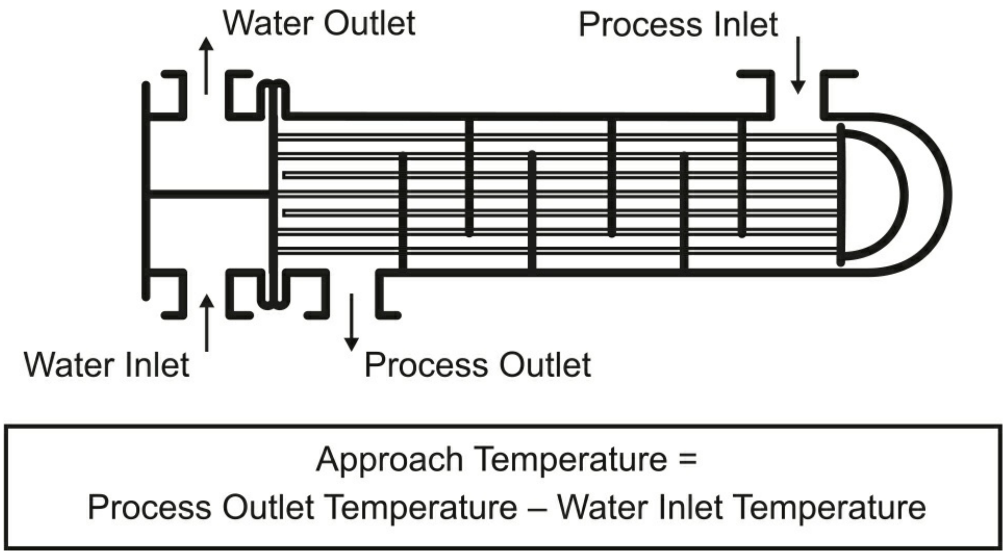

FIGURE 14.11 Approach temperature can be calculated easily if water inlet and process outlet temperatures are available.

Terminal Temperature Difference (TTD)

This calculation is valuable in condensers, where further cooling below the condensation temperature is not desired. TTD is the difference between the gas condensing temperature and the cooling water outlet temperature, as shown in Fig. 14.12. The most common example of this is in steam condensers in electric utility plants, where minimal subcooling is desired, so that less heat is needed to create steam again from the condensate. In a steam condenser, TTD is the difference between the saturation temperature of the exhaust steam and the cooling water outlet temperature.

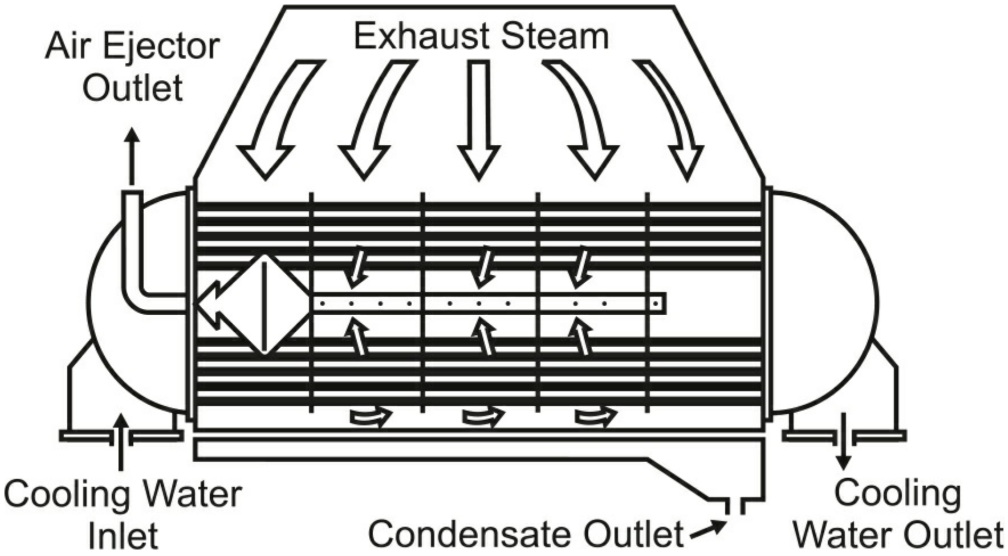

FIGURE 14.12 Terminal temperature difference (TTD) is the difference between the exhaust steam saturation temperature and the cooling water outlet temperature.

Reynolds Number

Water flow through a heat exchanger tube is not uniform. More water, at a higher velocity, moves through the center of a tube than at the tube wall. The water at the tube surface is flowing very slowly and is referred to as the static film of water (Fig. 14.13).

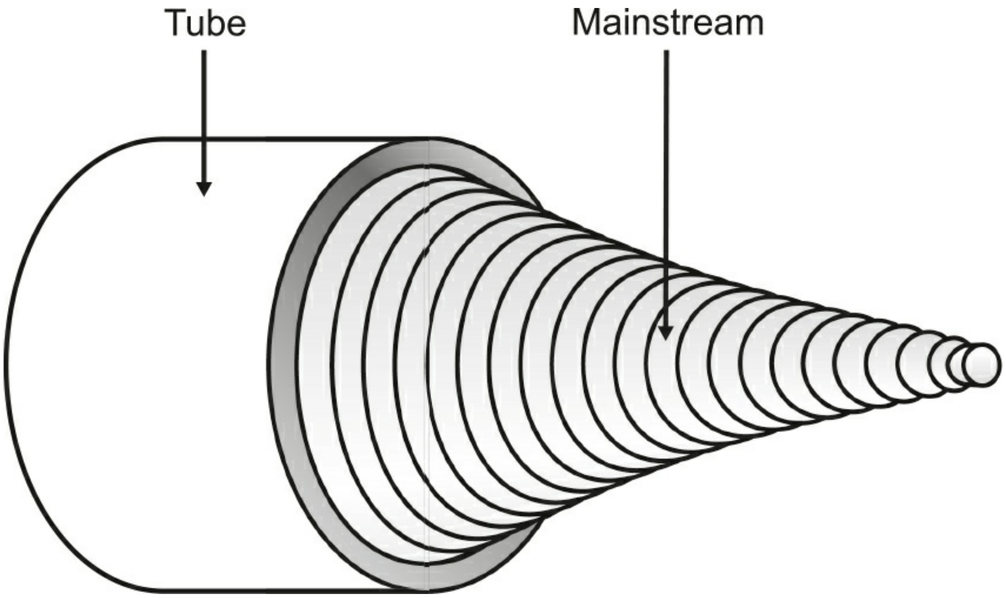

FIGURE 14.13 The water velocity profile in a tube will have the highest velocity at the tube center.

In addition to the velocity and mass flow differences between the center and surface of a heat exchanger tube, there is another important variable that must be considered: the nature of the flow. Fluid flow can either be laminar or turbulent (Fig. 14.14). Turbulent flow decreases the thickness of the static film next to the tube wall, promotes mixing, and increases the rate at which heat is absorbed by the cooling fluid.

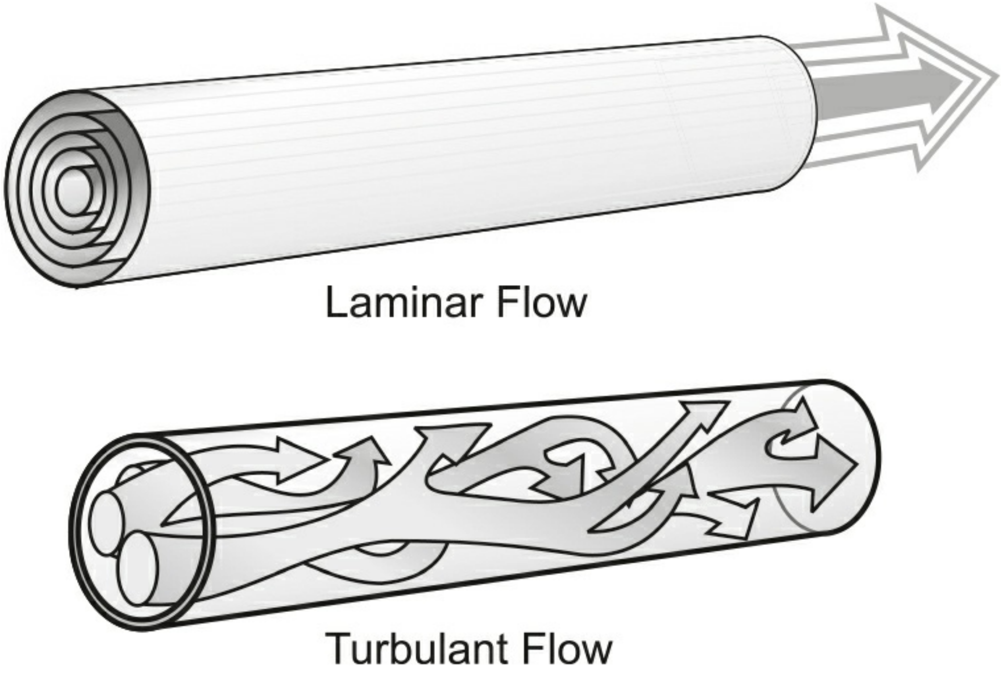

FIGURE 14.14 Laminar versus turbulent flow.

The Reynolds number is a dimensionless number that provides an indication of whether flow is laminar or turbulent. The Reynolds number can be calculated using Eq. (14.1) (U.S. units) or Eq. (14.2) (metric units):

$$R_e = d\nu/12\nu' \tag{14.1}$$

$$R_e = 100d\nu/\nu' \tag{14.2}$$

where R_e = Reynolds number (dimensionless)
d = tube inside diameter (ID), in. (cm)
ν = liquid velocity, ft/s (m/s)
ν' = liquid kinematic viscosity, ft^2/s (cm^2/s)

An example calculation of the Reynolds number for a heat exchanger with tube ID of 0.787 inch (2 cm) and velocity of 3.3 ft/s (1 m/s) is shown. The liquid is water at 100°F (38°C) with kinematic viscosity of 7.33×10^{-6} ft^2/s (6.811×10^{-3} cm^2/s).

U.S. Units

$$R_e = (0.787 \text{ in.})(3.3 \text{ ft/s})/[(12)(7.33 \times 10^{-6} \text{ ft}^2\text{/s})] = 29500$$

Metric Units

$$R_e = (100)(2 \text{ cm})(1 \text{ m/s})/(6.811 \times 10\text{-}^{3} \text{ cm}^2\text{/s}) = 29\ 400$$

As stated previously, the purpose in calculating the Reynolds number is to determine whether the flow through a tube is laminar or turbulent. The guidelines that follow apply to the majority of cases:

- If *Re* is less than 2100, flow is laminar.
- If *Re* is 2100 to 4000, flow may be laminar or turbulent.
- If *Re* is greater than 4000, flow is turbulent.

Coefficient of Heat Transfer (*U*-value)

The coefficient of heat transfer, or *U*-value, is one of the best indicators of heat exchanger performance and efficiency. *U*-value is much less sensitive to changes in process flow, process temperature, and coolant temperature than many of the other indicators commonly used. Except for extreme changes in process flow or temperature, increases or decreases in *U* will usually reflect real differences in the cleanliness of the exchanger. However, changes in *U* can reflect changes in the cleanliness of the process side as well as the water side (Fig. 14.15).

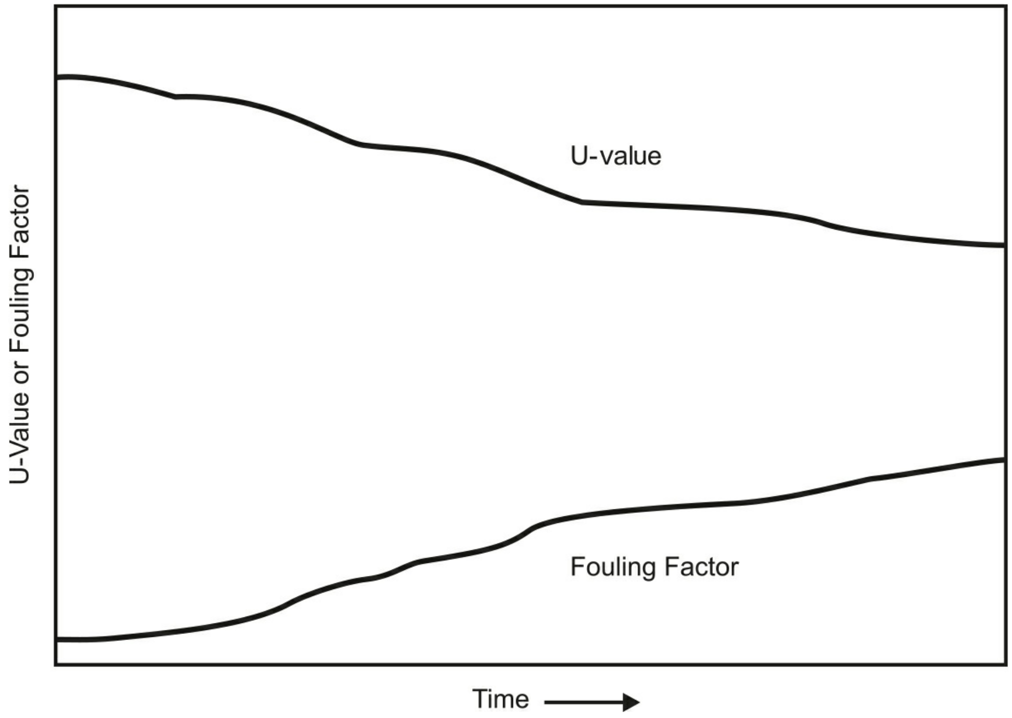

FIGURE 14.15 Decreasing *U*-value can indicate fouling in an exchanger. A fouling factor trend curve for a heat exchanger is the inverse (reciprocal) of the *U*-value curve.

The heat transfer coefficient or *U*-value is calculated using Eq. (14.3).

$$U = Q/[(A)(\text{LMTD})] \tag{14.3}$$

where U = heat transfer coefficient, Btu/[h · ft² · °F] (kW/[m² · °C])
Q = heat duty, Btu/h (kJ/h or kW)
A = heat transfer area of exchanger, ft² (m²)
LMTD = log mean temperature difference, °F (°C)

Note that a correction factor is usually applied to LMTD for multi-pass exchangers, based on the configuration of the exchanger.

Normally, heat exchangers will have *U*-values in specific ranges depending on the type of fluids on both sides of the exchanger and whether condensation is involved. Here are typical *U*-value ranges for different heat exchange processes:

- *U*-value range for gas-liquid heat exchange is 50 to 150 Btu/[h · ft^2 · °F] (0.3–0.9 kW/[m^2 · °C]).

- U-value range for liquid-liquid heat exchange is 100 to 300 Btu/[h · ft^2 · °F] (0.6–1.7 kW/[m^2 · °C]).
- U-value range for condensers is 400 to 600 Btu/[h · ft^2 · °F] (2.3–3.4 kW/[m^2 · °C]).

Fouling Factor

The fouling factor for any heat exchanger, is a measure of how the present coefficient of heat transfer compares with either the design coefficient of heat transfer, or the coefficient of heat transfer immediately after the exchanger was cleaned down to the bare metal on both the water and the process sides. Fouling factor is calculated using Eq. (14.4).

$$f = 1/U_c - 1/U_d \tag{14.4}$$

where f = fouling factor, [°F · ft^2 · h]/Btu ([°C · m^2]/kW)
U_d = U-dirty, Btu/[h · ft^2 · °F] (kW/[m^2 · °C])
U_c = U-clean, Btu/[h · ft^2 · °F] (kW/[m^2 · °C])

Typically, fouling factors are in the range of 0.001 to 0.005 [°F · ft^2 · h]/Btu (0.18–0.88 [°C · m^2]/kW).

If a design U or a design fouling factor is not available for a given exchanger, fouling factor can still be calculated. The design U may be calculated by using the process flow, process temperature, and water temperature originally specified for the exchanger. Subtracting the reciprocal of this U-design from the reciprocal of the present U-value for the exchanger will yield the present fouling factor with a reasonably high level of accuracy in most cases. Corrected LMTD should be used in the calculations.

C Factor

C factor is a calculation to relate flow through an exchanger to the pressure drop (ΔP) available across the exchanger. Flow through a clean exchanger is related to the DP by Eq. (14.5).

$$F = (C_{\text{clean}})(\Delta P^{0.5}) \tag{14.5}$$

where F = flow, gpm (m^3/h)
C_{clean} = constant calculated from design flow and clean ΔP
ΔP = Pressure drop across the exchanger due to the flow, psig (kPag)

Rearranging the formula, C factor is variable and is calculated from the actual flow and ΔP. This variable C factor (called C_{foul}) now indicates the loss of heat transfer as fouling occurs and is calculated using Eq. (14.6).

$$C_{foul} = F/(\Delta P^{0.5}) \tag{14.6}$$

Some points to remember about the C factor are:

- C factor is not dimensionless and will be dependent on the design flow and calculated clean pressure drop at design flow.
- C factor is a function of the cleanliness of the exchanger tubes. The C factor will decline with time, if fouling or scaling result in narrowing of the inside diameter of the tube.
- C factor is suitable for monitoring tube-side cooling water exchangers with tube outside diameter (OD) of less than 1.0 inch (25.4 mm).
- In some cases, shell-side cooling water geometry will also show a decrease in C factor, if uniform scaling or fouling causes narrowing of the spaces between the tubes.
- Neither tube-side nor shell-side cooling water will show a significant decrease in C factor, if only silting of the exchanger occurs and ΔP does not change.

The design clean ΔP is calculated using the design flow and clean heat exchanger geometry. The actual differential pressure (ΔP) is determined by the total hydraulics, including the circulating water pumps and throttle valves in the system. If gauges are used to measure actual ΔP, each gauge reading must be corrected for the difference in elevation above a common point. Figure 14.16 illustrates how the correction to pressure reading is done, if the gauges are at different elevations. Only one of the two pressure readings must be corrected.

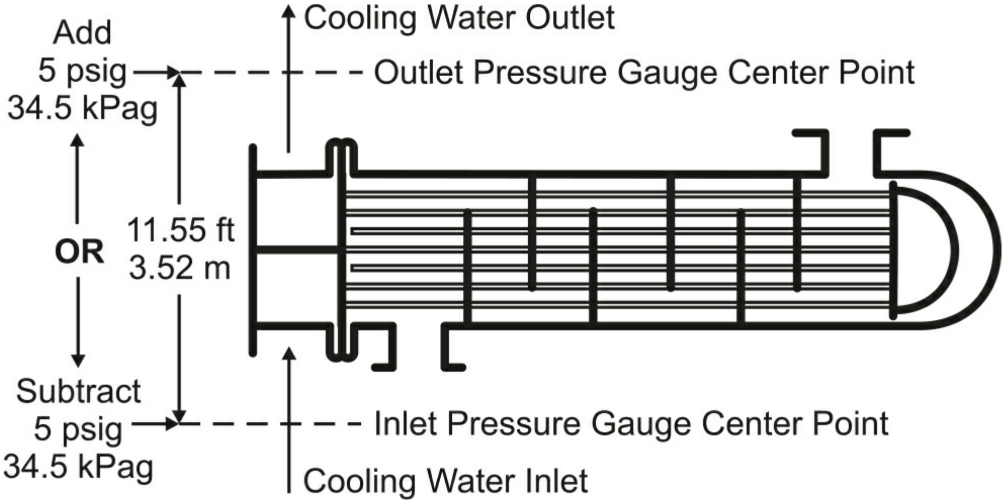

FIGURE 14.16 For every 2.31 ft (0.70 m), 1 psig (6.9 kPag) must be added to the value from the upper pressure gauge or subtracted from the value from the lower pressure gauge.

Skin Temperature and Water Velocity

As mentioned in the beginning of this chapter, skin temperature and water velocity in the exchanger are critical parameters for determining the stress in any cooling system. Skin temperature and water velocity are difficult to calculate and beyond the scope of this book. These parameters depend on characteristics of the exchanger, such as whether water is on the tube or shell side and whether the water and process flow co-currently or counter-currently through the exchanger. These values are often specified as part of the design characteristics of a heat exchanger. These parameters should be determined under current operating conditions to compare to the design specifications.

Cooling water temperature varies throughout the cross section of a tube; the hottest water is nearest the tube wall. The temperature of the tube wall, called the skin temperature, is important in selecting chemical treatment programs. In fact, skin temperature is the most important variable controlling corrosion and deposition on the tube surface. The skin temperature is defined by water velocity, heat flux, water temperature, process temperature, and thermal conductivity of the tube wall. Areas of high skin temperatures [above 200°F (93°C)] are the most probable locations for scale formation and corrosion. Many compounds found in water-formed deposits are less soluble at increased temperature, and corrosion reactions proceed faster as temperature increases.

Effects of Corrosion and Deposits

Problems created by the interaction of the water and cooling system components can reduce the efficiency of the heat transfer process. These problems include corrosion of system metals and deposition on surfaces in heat exchangers, system piping, or the cooling tower. Deposition can be due to corrosion products, scale-forming minerals, suspended solids, and bacteria in the water. Both thermal and hydraulic performance of a cooling system is decreased by deposition. More details on these problems can be found in Chap. 15 on Cooling Water Deposition, Chap. 16 on Cooling System Corrosion, and Chap. 17 on Cooling Water Biology.

Corrosion and deposition affect the efficiency of the cooling system. If corrosion and deposition are not kept under control, heat exchangers will soon become inefficient, and equipment will be ruined. Efficiency loss and equipment failure cost money in terms of increased maintenance, equipment repair, or replacement, or lost production. In extreme cases, safety problems that cost jobs or lives may result. Examples of these problems include the following:

- Reduced heat transfer efficiency—Clean heat exchangers, free of corrosion and deposits, allow a plant to operate at peak production. Corrosion and deposition on heat transfer surfaces reduce the ability to remove heat from the process. Production goes down while operating costs go up.
- Increased maintenance and cleaning—Corrosion products and other deposits cause fouling in heat exchangers and transport piping. The standard way to remove deposits is to take the system off-line for cleaning. System cleaning requires time and personnel to do the job right. Time is money when a unit is out of production.
- Equipment repair and replacement—If corrosion is severe, system piping or heat exchanger tubes may develop leaks. Again, the system operation must be stopped for repair. Some heat exchanger tubes may be taken out of service by plugging the tube. With others, the only choice is to re-tube or replace the entire exchanger, which is a costly operation.
- Process-side or water-side contamination—When leaks occur because of corrosion, serious problems result on both sides of the heat exchanger. Cooling water may leak directly into the process stream,

contaminating product, leading to loss of production and wasted product. Disposal or rework of contaminated product can be very expensive. The process stream leaking into the cooling water may create even more deposits, fouling, and corrosion.

- Unscheduled shutdown—Corrosion and deposition in the cooling system can unexpectedly stop operation of an entire plant. The cost of water, maintenance, and system repair seems small, when compared to the dollars lost due to the loss of production.

The net impact of poorly controlled corrosion and deposition is increased operating costs and reduced profitability for any facility with a cooling system. However, there are some examples of fouling that are normal or not always caused by interaction of the water and the system components.

Normal Surface Film Formation

A normal loss in heat transfer will occur when a new or recently cleaned exchanger is put in service. A surface film will form on a clean tube, even under normal, well-inhibited conditions. The tube narrows in diameter as the deposit forms, and the velocity of the cooling water increases. This surface film of deposit will decrease the cooling water skin temperature because of the insulating effect of the film. The increased flow also tends to decrease the skin temperature and retards further formation of deposits. If the exchanger is sized properly, the exchanger performance will normally plateau at a capability that will economically satisfy the process requirements. In most cases, heat exchangers are oversized by design to account for this normal deposition. This leveling of performance indicates an acceptable treatment program is in place. More than 85% of the exchangers in a unit should operate three to four years before cleaning. However, if further deposition occurs, the performance of the exchanger will suffer as *U*-value decreases with greater deposit thickness.

Mechanical Causes for Plugged Tubes

Trash, pieces of broken fill, pieces of scale, or corrosion products will deposit on the tube sheet, plugging tubes and thereby reducing heat transfer area and cooling water flow. Proper backwashing techniques will recover the lost performance but must be done on a scheduled basis. Backwashing should be timed to occur before significant performance loss is noted. Additional equipment including Y-strainers, basket strainers, and special strainers installed in the inlet of the exchanger may be required in severe cases.

Types of Cooling Water Systems

Heat transferred to the water from the process in a heat exchanger must then be rejected to the environment. This is the role of the cooling water system. There are three basic types of cooling water systems: once-through, closed recirculating (nonevaporative), and open recirculating (evaporative) systems. The type of cooling system defines how the heat is rejected to the environment.

In nonevaporative systems like once-through and closed cooling water systems, heat rejection is governed by the specific heat capacity of water (1 Btu/[lb · °F] or 4.19 kJ/[kg · °C]). In a cooling tower system, where water is evaporated, the phase change from liquid to gas dissipates about 1000 Btu/lb (2300 kJ/kg) of water converted to vapor. Evaporative systems can dissipate 50 to 100 times more heat to the environment per unit of water than a nonevaporative system.

A short description of each cooling water system is given as follows. Open recirculating cooling tower systems are covered in more detail, because these systems are the most dynamically complex.

Once-through Cooling Water Systems

Once-through water is taken from the water source, passed through the cooling system, and returned to the receiving body of water. Heat picked up from the process is rejected by nonevaporative cooling. Heat picked up in the once-through water is often beneficial for process use, such as in Paper Mills, reducing the need for heating the water by other means. The chief characteristic of once-through cooling water systems is the relatively large quantity of water used. A simple flow diagram for a once-through cooling water system is shown in Fig. 14.17. Some once-through systems use plant water for drinking as well as cooling, thereby requiring chemical treatment that is safe for potable use.

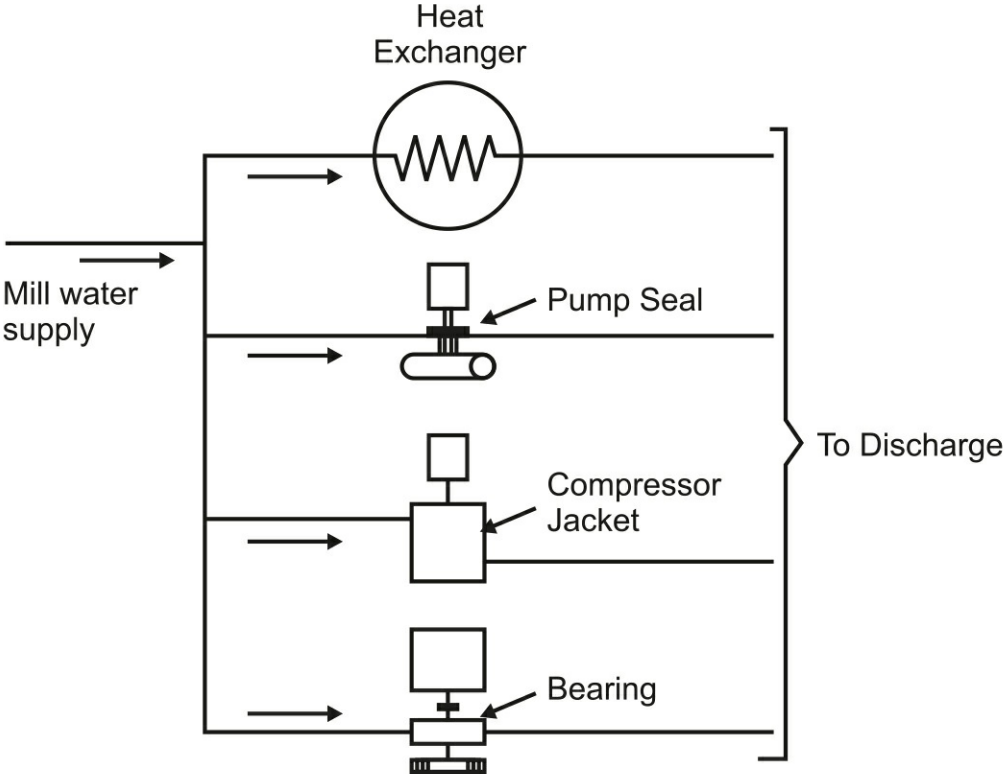

FIGURE 14.17 Typical service for a once-through cooling system.

There are many examples of once-through systems, although not all of these applications are cooling systems. The use of once-through cooling water has decreased due to the environmental effects of the discharge and inability to treat the systems economically for corrosion and deposition. In some parts of the world, once-through systems may be used in electric utilities, paper mills, refineries, chemical plants, and steel mills.

Examples of Once-through Systems

Many industries use water as an essential component of the manufacturing process in addition to cooling purposes. In some cases, the volume of water usage is a large part of the process. Many food industry processes use water for washing at some stage of product processing. Examples of once-through cooling and process water applications are:

- Electric utilities—Condenser cooling is the largest water use in the power generation process. A utility may be situated on a river or use a large impounded lake as a once-through cooling water source. Process heat can be dissipated without having the expense of building and operating a cooling tower. An impounded lake is technically a recirculating cooling system; however, because of the large quantities of water involved, the system must be treated like a once-through system.

- Paper mill systems—Paper mills require large volumes of water for cooling plant equipment and the papermaking process. For example, the fiber slurry leaving the headbox on the paper machine is 99% water and only 1% fiber. Water availability and quality are essential components of paper manufacture. The same water system may supply both the cooling and process water.
- Steel mills—Large volumes of water are required in primary metals manufacture because of the cooling requirements of the molten metals. While some of these systems still use once-through water, many have been converted to recirculating systems with cooling towers. This conversion was necessary for environmental reasons.
- Food plants—Very stringent water quality specifications apply in the food industry, where rigorous regulations have been established to minimize possible adverse health effects. In this case, the impact of water quality on the process may be significant. In most cases, the potable water used for the process is kept separate from cooling water systems.
- Municipal or potable water systems—Facilities that produce drinking water for industry and residential communities must meet all potable standards for the particular country. While these are once-through systems, cooling applications are generally not involved. The main problems in these systems are corrosion and scaling of the system piping and iron and manganese contamination that reduces the water quality for the user.

Other types of systems may be occasional once-through systems. For example, most industrial facilities have firewater systems that are separate from normal operating processes. This water source may occasionally be used for makeup water to a cooling system or for wash water. However, the water is mostly held in a static condition within the system. Static or non-flowing systems present unique treatment challenges and are not covered in this chapter.

Cooling Lakes or Ponds

Man-made lakes are sometimes used for electric utility condenser cooling, particularly in the United States. These lakes are often created by building a dike around a large area of land. This area is then filled with water from a river. The lake may also be called impounded or perched lakes. The total water volume of the lake system is such that the condenser cooling water must be treated like a once-through system. However, these lakes recycle the water used for cooling. Makeup is often drawn from a river and there may be no blowdown, other than seepage through the lake bottom. Some cooling of the lake occurs by heat loss to the environment and some by direct evaporation from the surface of the water. Dissolved salts in man-made lake water can slowly concentrate above the concentration of the makeup water. The concentration effect may be higher in summer than in winter, if evaporation rates are different.

The pH and alkalinity of the lake can be affected by a number of factors. As the lake water concentrates, the typical dissociation of bicarbonate (HCO_3^-) into carbonate (CO_3^{-2}) and carbon dioxide (CO_2) can occur. (See Chap. 4 on Water Chemistry for an understanding of alkalinity relationships.) Some of the CO_2 will be lost to the atmosphere by equilibration, driving up the lake water pH. During daylight hours, algae can consume some of this CO_2 by photosynthesis, further pushing the bicarbonate/carbonate equilibrium to produce higher carbonate levels and higher pH. Respiration of bacteria and other oxygen consumers will release CO_2, but generally not enough to counterbalance the effect of algae. The net impact may create diurnal cycles, where pH increases during daylight hours and decreases at night. Alkalinity and pH levels can increase to the point where calcium carbonate scale formation is a problem.

Problems in Once-through Systems

Water-related problems can be unique in once-through systems, because of the large volume of water used and specific characteristics of the water source. There are two main sources of water—groundwater and surface water.

Water pumped from below the surface of the earth using a well is groundwater. Groundwater characteristics vary depending on the type of rock below the surface that surrounds the water. Groundwater generally has higher levels of dissolved minerals than surface water at the same locale (Table 14.1). The reason is that groundwater has a very long contact time with the minerals in the ground. In some areas, the higher dissolved solids can be corrosive ions like sulfate and chloride. In other areas, the mineral content may be calcium, magnesium, and high alkalinity that can form scale in a cooling system. High silica concentrations exist in well water in localized parts of the world. Silica can cause either amorphous silica scale or magnesium silicate scale, depending on the other characteristics of the water and the system. Some wells have high amounts of dissolved gases like CO_2 or hydrogen sulfide (H_2S) that can be corrosive. Metal ions like iron and manganese are often present as soluble ions in groundwater sources. These metal ions may be oxidized to insoluble forms after the water is brought in contact with air and precipitate in cooling systems.

Constituent (mg/L Except Conductivity)	Well Water Ames, IA, U.S.	Green Valley Lake Creston, IA, U.S.
Calcium ($CaCO_3$)	360	89
Magnesium ($CaCO_3$)	170	60
Total hardness ($CaCO_3$)	530	149
Iron (Fe)	2.2	1.7
Manganese (Mn)	0.41	0.1
Silica (SiO_2)	27	7.2
Sodium (Na)	41	11
Chloride (Cl)	92	12
Sulfate (SO_4)	160	11
M alkalinity ($CaCO_3$)	330	120
P alkalinity ($CaCO_3$)	<1	<10
Conductivity (µS/cm)	1200	300

TABLE 14.1 Groundwater and Surface Water in a Similar Geological Region

Surface water quality is not as uniform as groundwater. In fact, the variability of surface water is the major challenge for industrial water treatment applications. Suspended solids or turbidity in a surface water supply is highly variable, with rapid changes possible depending on upstream or climatic events. Variations in turbidity require a flexible treatment program to handle the variable foulant loading. Temperature variability occurs seasonally, but also in much shorter periods, depending on conditions upstream from point of use. Subcooling of the process fluid may occur if water temperature is too cold, resulting in throttling (reducing) cooling water flow through an exchanger. Throttling the water flow can cause an increase in fouling due to the low water velocity. Cooling capacity may be impossible to recover, when the source water becomes warmer again and water flow through the exchanger is increased.

Seawater and brackish water are unique water sources that can contain high dissolved solids, mostly consisting of sodium and chloride ions. Because the high dissolved solids can be very corrosive, heat exchangers or condensers are normally made of corrosion resistant alloys like aluminum brass or metals like titanium. Distribution lines are normally coated mild steel or nonmetallic materials. Seawater is generally very consistent around the world. The total dissolved solids (TDS) range of seawater is 34 to 36 g/L in most oceans. Brackish water may come from surface or groundwater sources. Brackish water can contain 0.2 to 50 g/L total dissolved solids or more. Some well waters can be considered brackish, due to high concentrations of sodium carbonate or sodium chloride present in the water (Table 14.2).

Constituent (mg/L Except Conductivity)	Deep Well Bridgeport, TX, U.S.
Barium (Ba)	14
Boron (B)	10
Calcium ($CaCO_3$)	5500
Magnesium ($CaCO_3$)	1300
Total hardness ($CaCO_3$)	6800
Iron (Fe)	4.4
Manganese (Mn)	1.3
Potassium (K)	220
Silica (SiO_2)	<26.1
Sodium (Na)	12 000
Strontium (Sr)	380
Chloride (Cl)	25 000
Sulfate (SO_4)	57
M alkalinity ($CaCO_3$)	2700
P alkalinity ($CaCO_3$)	1100
Conductivity (µS/cm)	62 000

TABLE 14.2 Example of Brackish Well Water Composed Primarily of Sodium Chloride

Unique biological problems can result from the use of groundwater or surface water in once-through systems. Well water can contain anaerobic bacteria that can cause localized corrosion. Surface water, particularly seawater, presents problems from growth of macro-organisms like clams or mussels in a cooling system. The control of large species (macro-organisms) in once-through water systems is very challenging. The organisms can grow rapidly once attached to a cooling system. Macrofouling can cause damage to pumps, restrict water flow, and plug heat exchanger tubing, resulting in lost cooling capacity. See Chap. 17 on Cooling Water Biology for more information on macrofouling.

Closed Recirculating Systems

Closed recirculating systems are generally very simple. However, these systems can become the most difficult to maintain once problems occur. A closed recirculating system is one in which the water is circulated in a closed loop with negligible evaporation, exposure to the atmosphere, or other influences that would affect the chemical or biological properties of the system water. In closed recirculating systems, heat is transferred to the cooling water from the hot process, and then the heat is transferred from the cooling water to the environment in another piece of heat transfer equipment (Fig. 14.18). In closed cooling systems, the heat is usually dissipated by an open recirculating cooling system or by air-cooling in a fin-fan cooler.

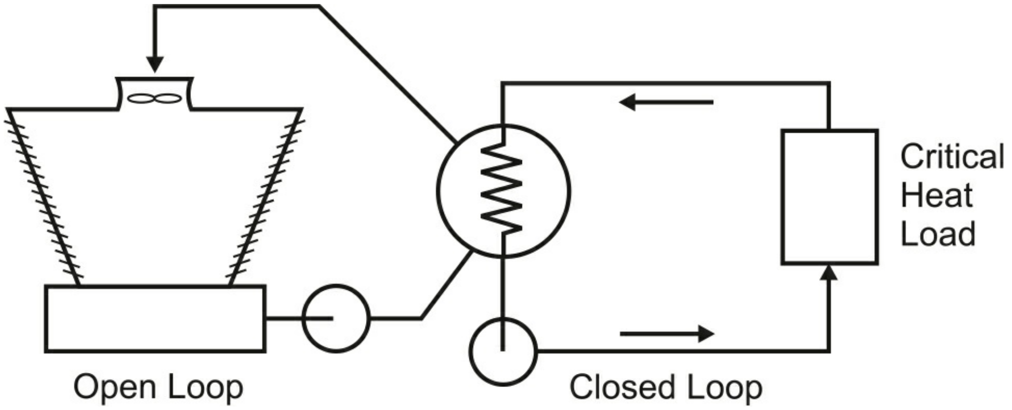

FIGURE 14.18 A closed cooling system is often used for critical heat transfer applications. In this case, the closed system water is cooled by an open cooling tower system.

Closed System Characteristics

There are many different types of closed systems used in a wide variety of applications, from building heating and cooling to primary metals applications. Example criteria that define when a closed system is used instead of an open system include:

- A critical process, where cooling water system failure creates serious problems.
- An extremely hot process, where scale formation on heat transfer surfaces must be eliminated.
- A coolant temperature below ambient or below 32°F (0°C) is necessary.
- A water temperature above boiling is required (e.g., pressurized hot

water systems).

- A higher degree of control is required.

Closed cooling systems can be used in refrigeration systems with temperature below freezing, or for cooling high heat flux systems like a continuous steel casting mold. Closed cooling systems may have unique characteristics such as:

- The systems contain a variety of metals, often connected together forming galvanic couples. (See Chap. 16 on Cooling System Corrosion.) Metals include mild steel and copper alloys, with occasional use of aluminum, stainless steel, etc.
- Systems are designed for minimal makeup and blowdown but do not often achieve minimal water losses.
- Since these systems are not designed for blowdown, filtration of the recirculating water is recommended.
- System volumes range from as small as 10 gal (0.04 m^3) to more than seven million gallons (26 500 m^3).
- Some systems are operated with intermittent idle periods, where no water flow exists.

Problems in Closed Recirculating Systems

Closed cooling water systems suffer the same problems as other cooling water systems, that is, corrosion, deposition, and microbial growth. The major performance-related problems in closed systems are most often due to water leakage or microbial problems. Corrosion can usually be controlled to very low rates of metal loss, because inhibitor treatments can be maintained at high dosages. Similarly, scale can be minimized by use of softened makeup water. However, water loss from leakage or microbial degradation of inhibitors can cause increased corrosion and scale.

Theoretically, under the conditions that exist in a truly closed recirculating system, all of the common scale-forming constituents in the system water (such as calcium carbonate, calcium sulfate, magnesium salts, and silica) can deposit on metal surfaces without any noticeable results because such small quantities are involved. However, in the more typical system, water leakage creates demand for more makeup water that brings additional scale-forming ions into the closed system water. Continued precipitation with each new increment of water added to the system can cause significant scale formation, plugged water passages, and reduced heat transfer.

It may seem that because the average closed system sees little sunlight, has low oxygen content, and contains few nutrients, there should be no problem with microbial growth. In reality, microbial growth can be severe for several reasons. Leakage causes higher makeup rates, which introduces more oxygen, debris, and nutrients and inoculates the system with new microbial organisms. Process leaks can provide high amounts of food for microorganisms. Many closed systems have tanks that are open to the atmosphere, or have entrainment of air at seals, so oxygen levels can be at or close to saturation. Finally, some microbial organisms can use some corrosion inhibitors like nitrite as a food source. All of these factors illustrate how microbial problems can occur in closed cooling water systems. Microbial problems contribute to fouling, corrosion, and loss of heat transfer. In fact, biofilms are among the most insulating deposits encountered on heat transfer surfaces (refer to Fig. 14.5 shown earlier).

Another problem is that closed cooling systems are rarely equipped with continuous monitoring or automated control systems. This situation may lead to neglect of the system, because of the false impression that system conditions and product dosage should be constant. However, system conditions can change quickly due to leakage or microbial contamination. For this reason, continuous monitoring and control systems, are very valuable for best results and lowest total cost of operation.

Open Recirculating Systems

An open recirculating system incorporates a cooling tower, evaporative condenser, or evaporation pond to dissipate the heat removed from the process or product. An open recirculating system (Fig. 14.19) takes water from a cooling tower basin or pond, passes the water through process equipment requiring cooling, and then returns the water through the evaporation unit, which cools the water that remains. The open recirculating system repeats this process of reuse, taking in sufficient freshwater makeup to balance the water evaporated and water blown down from the system to control the chemical character of the recirculating water. This reuse of water greatly reduces water demand (e.g., withdrawal from a river) and discharge or blowdown. With the severe water availability issues that we face today, reducing the amount of water used as makeup to cooling towers is a major concern, and the focal point of many innovations in water treatment.

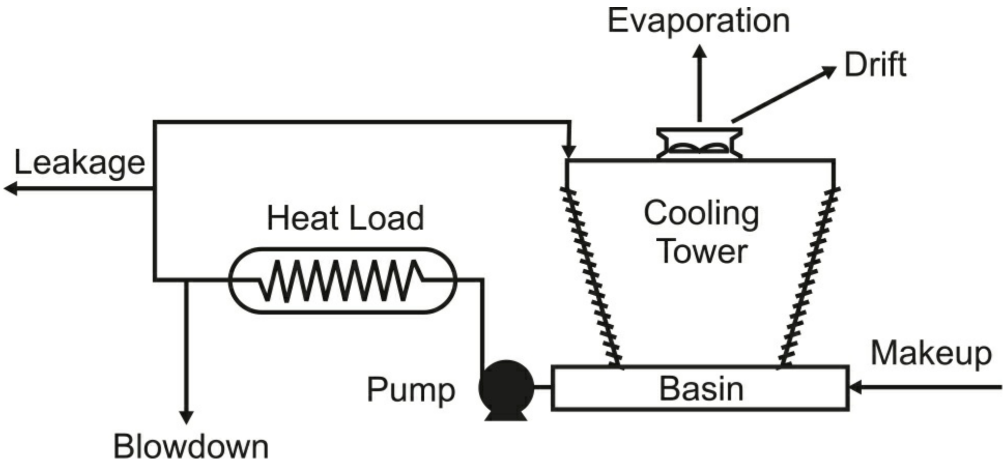

FIGURE 14.19 Typical open recirculating system using a cooling tower for heat rejection by evaporation of water to the atmosphere.

Cooling Tower Systems

These common open recirculating systems are designed to evaporate water by intimate contact of water with air. Cooling towers are classified by the method used to induce airflow (natural or mechanical draft) and by the direction of air flow (counterflow or crossflow relative to the downward flow of water). The basic components of a crossflow cooling tower are shown in Fig. 14.20. These components are common to most cooling towers, but the configuration may be different in other cooling tower designs.

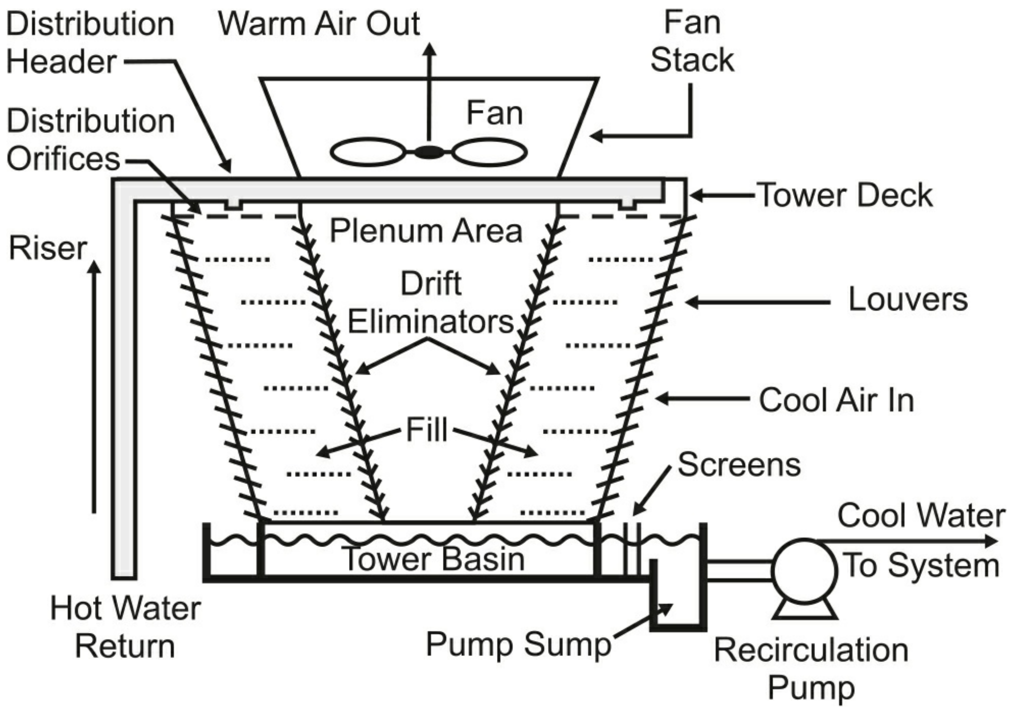

FIGURE 14.20 Example of the basic components of a cooling tower (crossflow) that create the contact between air and water to cause evaporation and cool the water.

Airflow in natural draft towers is created by the difference between air density inside the tower and the surrounding atmosphere. The warmer, more humid air inside the tower has lower density, which establishes the airflow. Wind velocity also affects performance. Most natural draft towers in modern utility service are of hyperbolic design. These tall towers provide cooling without fan power and minimize plume problems and drift.

Mechanical draft cooling towers use fans to move air, instead of depending on natural draft or wind. This speeds the cooling process and increases the efficiency of the tower by increasing the air velocity over droplets of water falling through the tower. Mechanical towers can, therefore, evaporate much more water than natural draft towers of the same size. There are two designs of mechanical draft towers, forced and induced draft. Fans mounted on the side of forced draft towers, force air through the tower packing, mixing air with the falling water (Fig. 14.21).

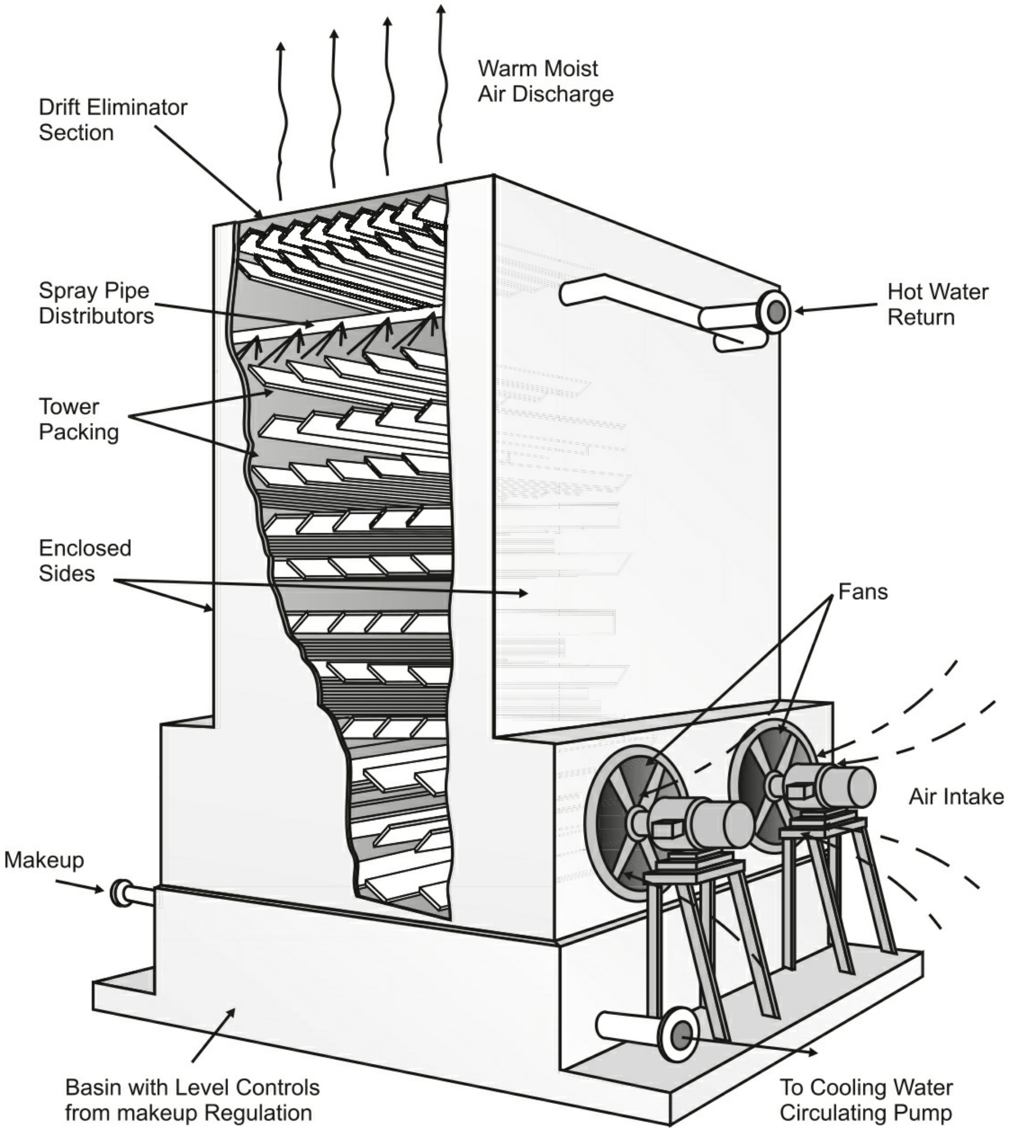

FIGURE 14.21 Forced draft cooling towers have the fans blowing air into the tower.

Induced draft cooling towers are either counterflow or crossflow with fans on top of the tower pulling cooling air up through or horizontally across the falling water. Figure 14.22 shows examples of counterflow and crossflow towers. The choice between forced draft and induced draft is based on engineering considerations that take prevailing weather patterns into account. A major consideration is to avoid recirculation of the warm air discharge, which would greatly reduce tower performance. The main advantage of a counterflow tower is that the coldest water contacts the driest air, providing the most efficient evaporation.

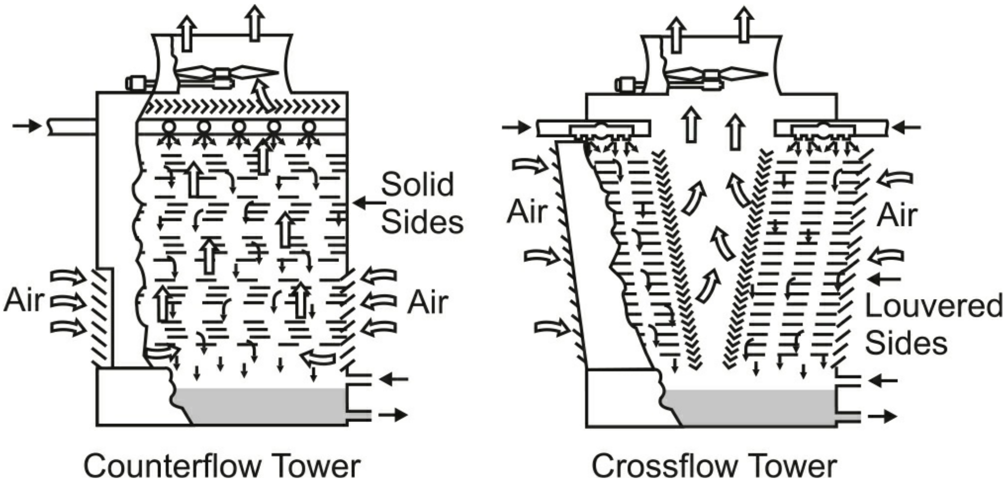

FIGURE 14.22 Examples of the two types of induced draft cooling towers.

The operating characteristics of cooling tower systems create a very dynamic environment. The factors that contribute to this dynamic nature include:

- Evaporation, which concentrates the ions in the water left behind
- The intimate exchange between water and air that can scrub contaminants out of the air
- Exchange of gases between the water and air
- Influx of fresh water, which is generally not treated to remove biological contaminants

All of these factors increase the challenges of effectively treating and controlling cooling tower systems. The first step in understanding the dynamic nature of cooling tower systems is to learn the calculations for the system dynamics.

Evaporative Condensers

Evaporative condensers are a special subset of wet evaporative cooling towers. An evaporative condenser is a small evaporative cooling tower with the heat exchanger inside the tower. Often, a serpentine coil is used for the heat exchanger. The coil contains a fluid to be cooled or condensed. Water cascades over the outside of the coil, providing evaporative cooling for the fluid within the coil. Evaporative condensers are commonly used in refrigeration, especially ammonia systems, and in some industrial cooling applications. The advantage of evaporative condensers is that cooling can be accomplished in a single step, without the need for additional heat exchangers or pumping the cooling water to the location of the heat exchanger.

Evaporative condensers can have a number of different designs. The air and water can travel in the same direction (parallel) or in opposite directions (counterflow). Air can be drawn (induced) or pushed (forced) over the coil by a fan. Some evaporative condensers, called combined units, have both a coil section and a separate fill section. In combined units, most of the evaporation occurs in the fill section and away from the coil, reducing the scaling and fouling potential for the coil. Examples of two designs are shown in Figs. 14.23 and 14.24.

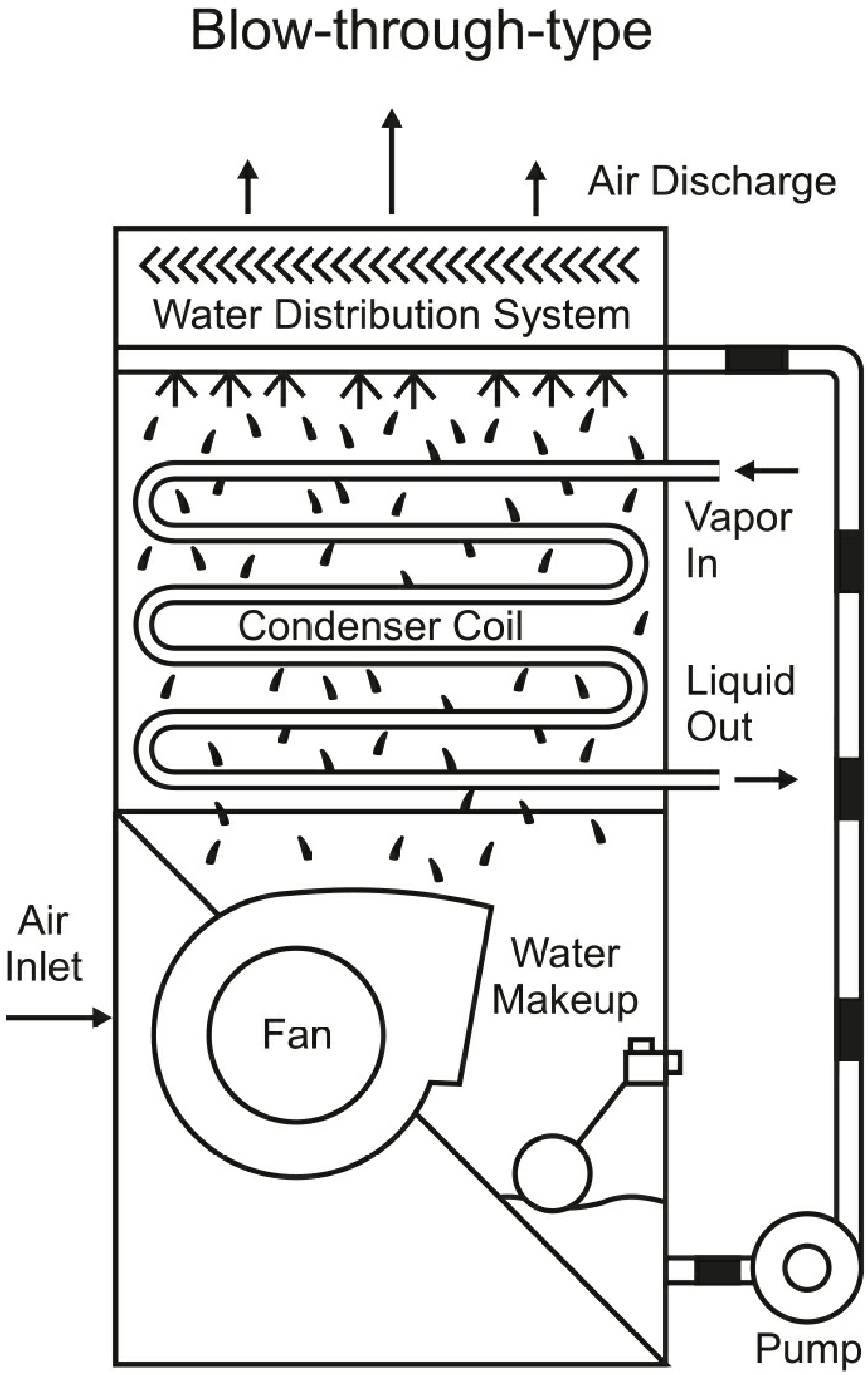

FIGURE 14.23 Blow-through-type evaporative condenser.

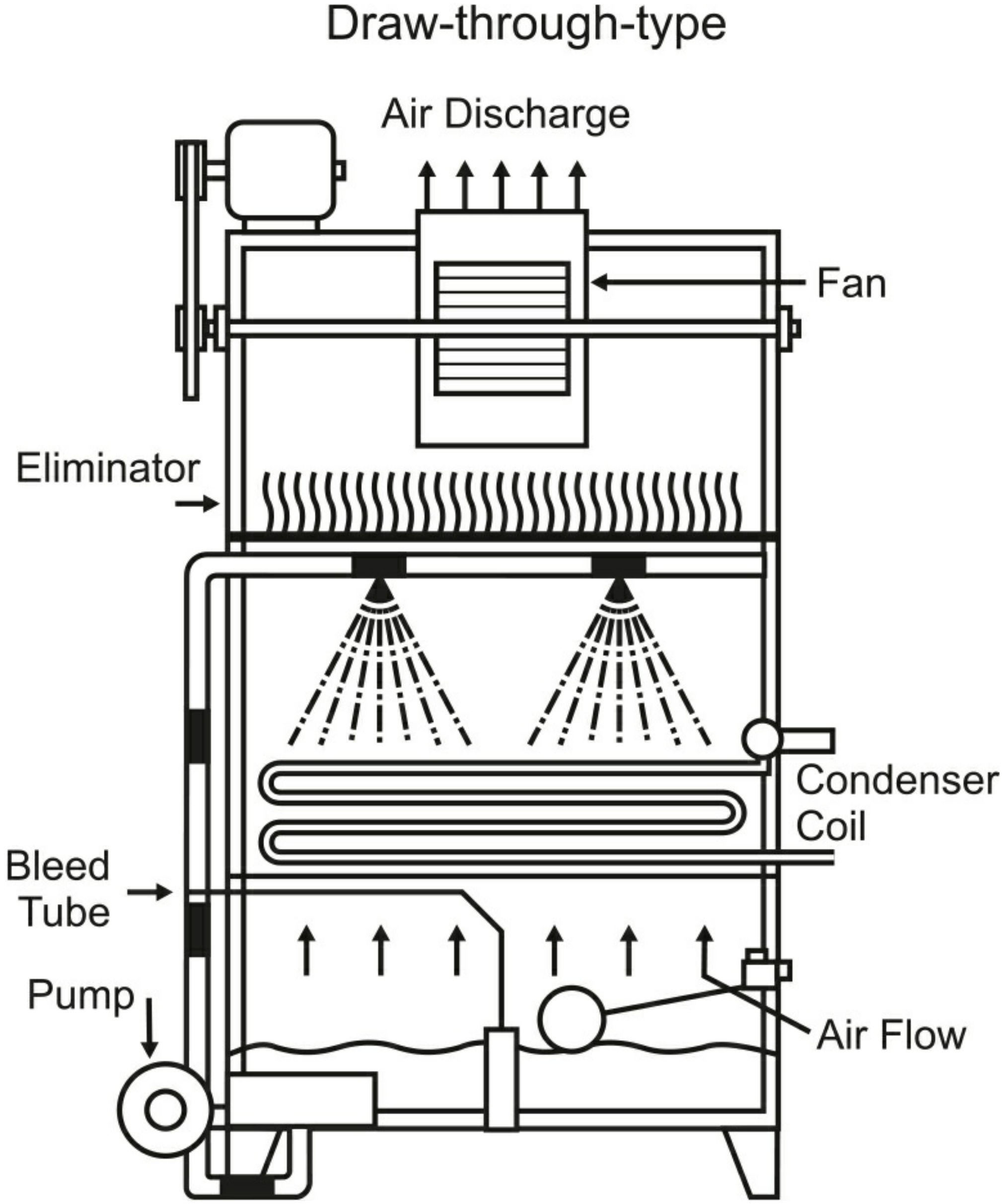

FIGURE 14.24 Draw-through-type of evaporative condenser.

Evaporative condensers experience the same problems as conventional open cooling tower systems with some notable additions. One of those problems is white rust from corrosion of galvanized components of the system. White rust is an unprotective deposit of zinc hydroxide or zinc carbonate on the surface of the metal. Evaporative condensers require thorough inspection of galvanized components. Any areas that show either total loss of the zinc coating or white rust should be noted. Both location and type of attack are important information. The presence of white rust can point to operation out of the desired control window of pH and alkalinity, or can point to improper passivation of a new or newly cleaned system. White rust is covered in more detail in Chap. 16 on Cooling System Corrosion.

Dry or Hybrid Tower Systems

The most widely used dry towers are commonly known as fin-fan coolers (Fig. 14.25). In most fin-fan coolers, the hot process liquid flows directly through the tubes, and air is blown over the outside of the tubes. These coolers do not use any cooling water.

FIGURE 14.25 A fin-fan cooler with two circular fans mounted under the bank of tubes that carries the hot process fluid. (*Courtesy of SPX Cooling Technologies, Inc.*)

Hybrid, or wet/dry, towers contain finned tubes in addition to normal cooling tower fill. In some of these towers, the hot, return water flows first through a set of tubes to reject heat without evaporation. The water then flows over normal cooling water fill to gain further cooling from evaporation. An example of this configuration can be seen in Fig. 14.26. In other configurations, the water can be diverted to flow either through the tubes or over the fill in the cooling tower. During colder weather, the cooling water is diverted through the tubes to provide nonevaporative cooling. During warmer periods, the water flows over the tower fill in an evaporative cooling mode. In either configuration, the tubes are susceptible to scaling, fouling, and corrosion.

FIGURE 14.26 A large combination wet-dry cooling tower used to cool condenser water at a utility station. (*Courtesy of the Public Service Company of New Mexico*.)

Spray Ponds

Spray ponds are large basins or pits filled with water with a spray system located just above the water surface. The water inlet distribution systems are equipped with headers that contain spray nozzles. Through the nozzles, hot recirculating water is sprayed into the air where water is evaporated, cooling the remaining water. Because of the relatively short air-water contact time, heat transfer efficiency is limited. Windblown water loss in spray ponds is high, but can be reduced by a louvered fence on the downwind side of the pond. Because ponds are open to the atmosphere, the water can collect considerable quantities of foreign matter. Pumping costs are less for spray ponds than for cooling towers, because of lower head requirements.

Treatment programs for spray ponds are similar to those for conventional wet evaporative cooling towers, because all of the same conditions generally apply. Spray ponds are different from cooling lakes (covered earlier in this chapter), which are generally more like once-through systems.

Open Recirculating System Calculations

There are simple relationships between the makeup rate, blowdown rate, evaporation rate, and concentration cycles of a cooling tower or evaporative condenser. Other calculations can be more complicated, particularly if greater accuracy is desired. Often, measured makeup or blowdown rates are not available. In this case, determination of the recirculation rate and the temperature drop (ΔT) across the cooling tower can be used to calculate other necessary variables. The definitions and equations that follow illustrate the main calculations necessary to define the operation of a system.

Recirculation Rate (*R*) This is the flow of cooling water being pumped through the entire plant cooling loop, usually cooling a number of heat exchangers. Simply using the pump nameplate data to determine recirculating rate can be misleading. Throttling valves, pipe restrictions, and head pressure restrictions can produce significant deviations from the nameplate values. The actual recirculation rate is seldom more than the nameplate data and frequently may be 10 to 20% less. A pump curve, usually available from the manufacturer, is more accurate than nameplate data. A pump curve plots recirculating flow against pressure increase across the pump. By measuring the pressure increase, a reasonably accurate flow rate can be determined. A diagnostic study using special tracers is a preferred approach to accurately measure flow rate.

Temperature Differential or Range (ΔT) The temperature drop of the water passing through the tower is called the delta T (ΔT) or “range” of the cooling tower. Temperature drop is determined by the difference between the temperature of the hot return water to the tower (T_1) and the temperature of the cold water in the tower basin (T_2), as shown in Eq. (14.7).

$$\Delta T = T_1 - T_2 \tag{14.7}$$

The ΔT is used in several calculations, such as the approximation of evaporation rate of the tower.

Approach Temperature The efficiency of a cooling tower can be measured by how closely the cold water temperature in the tower basin "approaches" the ambient wet-bulb temperature. The approach temperature is the difference between the cold water temperature and the wet-bulb temperature. For economic reasons, water cooling towers are designed to have an approach temperature of 5 to 10°F (3–6°C), in other words, to cool the recirculating water to within 5 to 10°F (3–6°C) of the ambient wet-bulb temperature.

While water cooling towers work against the wet-bulb temperature, dry cooling towers work against the dry bulb temperature.

Evaporation Rate (*E*) Evaporation is the water lost to the atmosphere in the cooling process. The evaporation rate is dependent on the amount of water being cooled (*R*), the heat load (ΔT), and the ambient air conditions. Evaporation can be calculated using Eq. (14.8).

$$E = f(R)(\Delta T)(C_p)/\lambda \tag{14.8}$$

where E = evaporation, gpm (m^3/h)
f = evaporation factor, decimal value of the percent of heat rejection due to evaporation
R = recirculation rate, gpm (m^3/h)
ΔT = water temperature difference across the tower, °F (°C)
C_p = water specific heat, Btu/[lb · °F] (kJ/[kg · °C])
λ = water latent heat of evaporation, Btu/lb (kJ/kg)

The latent heat of evaporation for water at normal temperature and pressure is about 1000 Btu/lb (2300 kJ/kg). The specific heat of water is 1 Btu/[lb · °F] (4.1868 kJ/[kg · °C]) at normal temperature and pressure.

If all heat loss is only from the latent heat of evaporation, then $f = 1$ in Eq. (14.8). However, some sensible heat loss always occurs in cooling towers. Sensible heat loss (by conduction through the piping, etc.) can amount to as much as 20% of the heat loss of the system. Additionally, using $f = 1$ does not take into account the impact of varying relative humidity or ambient air temperature on the efficiency of the tower. Low ambient temperature can reduce evaporation simply by the cooling effect of the cold air in contact with the water. High ambient air temperature can increase evaporation because additional water evaporates to cool the air going through the tower. Low air humidity will increase evaporation, while high humidity will decrease evaporation. These factors affect the amount of evaporation, such that *f* can be as low as 0.5, indicating that only 50% of the heat rejection is due to evaporation.

Therefore, a general rule of thumb is that 85% of the heat rejection is due to evaporation ($f = 0.85$). This factor is applicable in most cases and will give a good approximation of the evaporation rate (E). Remember, this rule of thumb represents an approximation only, and some error is possible, particularly at low ambient air temperature or low and high humidity. Ideally, calculation based on a measured makeup or blowdown rate and the system concentration ratio is better.

Concentration Ratio (CR) The concentration ratio or cycles of concentration (COC) for any cooling tower can be calculated by dividing the concentration of any ion in the recirculating water (C_{BD}) by the concentration of the same ion in the makeup water (C_{MU}), as shown in Eq. (14.9).

$$\mathrm{CR} = C_{\mathrm{BD}} / C_{\mathrm{MU}} \tag{14.9}$$

Alternately, if flows are accurately known, the concentration ratio can be determined by dividing the makeup flow rate (MU) by the total blowdown (BD) flow rate, as shown in Eq. (14.10).

$$\mathrm{CR} = \mathrm{MU} / \mathrm{BD} \tag{14.10}$$

The CR should be calculated for several individual components of the water to determine if the system is "in balance." In the ideal case, the system is in balance when the concentration ratios of all ions in the water (Ca, Mg, alkalinity, etc.) are equal (Table 14.3). Concentration ratios that are not equal can indicate that some mineral ($CaCO_3$, SiO_2, etc.) is precipitating from the recirculating water. For example, if the CR for calcium and alkalinity are more than 10% below the CR for magnesium, then $CaCO_3$ is probably precipitating in the cooling system. By knowing what may precipitate, the CR can be a valuable indicator that a problem is occurring.

Constituent (mg/L Except Conductivity)	**Makeup Water Corunna, Canada**	**Tower Water Corunna, Canada**	**Concentration Ratio**
Calcium ($CaCO_3$)	69	420	6.1
Magnesium ($CaCO_3$)	30	180	6
Sodium (Na)	7.7	77	10
Chloride (Cl)	13	100	7.7
Sulfate (SO_4)	19	510	27
M alkalinity ($CaCO_3$)	72	27	0.4
P alkalinity ($CaCO_3$)	<1	<1	—
Conductivity (µS/cm)	240	1400	5.8

TABLE 14.3 Example of Concentration Ratio Calculation from Tower and Makeup Water Analyses

The concentration ratios of some ions will be affected by chemicals added to the cooling system (Table 14.3). Acid for pH control, low or high pH products, bleach, chlorine gas, or other gases can affect both the alkalinity and CR of several ions in the cooling tower water. The CR for sulfate (SO_4^{-2}) would be increased when sulfuric acid (H_2SO_4) is added or where the plant atmosphere contains sulfur dioxide gas (SO_2). In these cases, the CR for alkalinity would be decreased, because alkalinity is destroyed by acid added to the tower. Chlorination of the cooling water will increase the CR for chloride (Cl^-).

The balance, of water evaporated, fresh makeup water added, and blowdown removed from the system, controls the concentration ratio. As CR increases from 1 to about 6, the amount of fresh makeup water is reduced (Fig. 14.27). At values of CR above about 6, the reduction of makeup demand is smaller. The lower limit for the makeup rate is the evaporation rate.

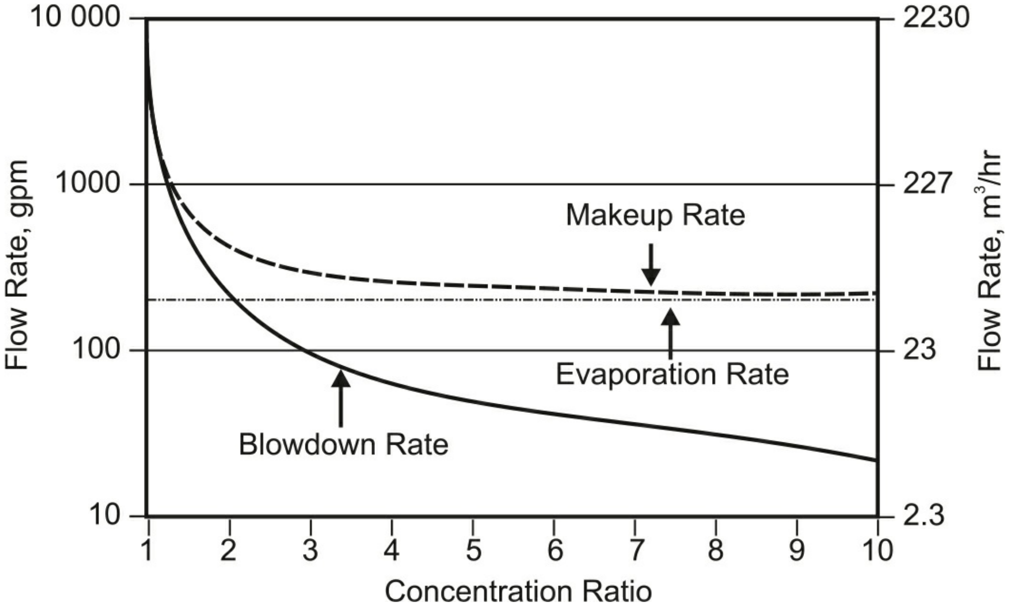

FIGURE 14.27 Reduction of makeup and blowdown rate as concentration ratio increases in a cooling tower.

Makeup (MU) Several expressions can be used to calculate the makeup rate. The simplest is the sum of the total system blowdown (BD) and evaporation rate (E).

$$\mathrm{MU} = \mathrm{BD} + E \tag{14.11}$$

The makeup rate can be calculated from total blowdown rate and the concentration ratio, if these two parameters are known.

$$\mathrm{MU} = (\mathrm{CR})(\mathrm{BD}) \tag{14.12}$$

If evaporation rate (E) and concentration ratio (CR) are known, the makeup rate can be calculated with Eq. (14.13).

$$\mathrm{MU} = (E)(\mathrm{CR})/(\mathrm{CR} - 1) \tag{14.13}$$

Blowdown (BD) Since pure water vapor is discharged by evaporation, the dissolved and suspended solids left behind concentrate. These solids would concentrate to brine, causing massive scale and corrosion, if there were no water loss other than evaporation. To balance this, controlled blowdown is discharged from the circulating system. Controlled blowdown (BD*C*) is calculated to remove solids at the same rate at which the solids are introduced by the makeup. There are other uncontrolled losses from the system. One is drift (*D*) and the other is leakage (*L*), sometimes deliberate, but usually accidental. These are included in the total blowdown (BD) calculation.

$$\mathrm{BD} = \mathrm{BD}_C + D + L \tag{14.14}$$

The total blowdown is related to other parameters as shown in Eqs. (14.15) to (14.17).

$$\mathrm{BD} = \mathrm{MU} - E \tag{14.15}$$

$$\mathrm{BD} = \mathrm{MU}/\mathrm{CR} \tag{14.16}$$

$$\mathrm{BD} = E/(\mathrm{CR} - 1) \tag{14.17}$$

Drift (*D*) Cooling towers are designed with equipment to reduce drift, typically using mechanical drift eliminators, as shown in the previous figures. Drift consists of the fine droplets of water that escape from the tower through the drift eliminators in the plenum area of the tower. Drift is included in the determination of total blowdown (BD) above. However, an estimation of drift losses can be made if the drift eliminator efficiency factor is known. In recent years this efficiency factor has improved significantly from 0.005 to 0.02% to as low as 0.0005% of the recirculating rate (*R*). This value can generally be found in the cooling tower specifications. If the actual efficiency factor cannot be found, drift (*D*) would be calculated as shown in Eq. (14.18), using the approximation of 0.01% of *R*.

$$D = 0.0001(R) \tag{14.18}$$

Leakage (*L*) Circulating water may be lost in the plant through pump or valve leaks; by once-through cooling of pump glands, compressor jackets, or bearings; or such uses as equipment or floor cleaning, when the cooling water line happens to nearby. In some plants, large miscellaneous usage of recirculating cooling water prevents operation above a concentration ratio of

1.2 to 1.5. This severely limits the economical chemical treatment of the system and prevents effective conservation of water.

Holding Capacity or Volume (*V*) Usually, most of the water in a system is contained in the cooling tower basin or spray pond. An approximation of the holding capacity can be obtained by calculating the volume of water in the basin and adding an extra 20 to 30% for the water contained in the pipes and equipment. Additional increases may be required if the system has an unusually large number of open box condensers, jacketed vessels, or holding tanks. Because of variability in cooling systems, this estimate can be very inaccurate.

System volume can be determined most accurately with a diagnostic study using special tracers. This can provide the system volume, total blowdown rate, and the holding time index in the same study. A known amount of inert tracer is added to the cooling system. The controlled blowdown should be turned off, if possible. After the steady-state concentration of the traced compound in the cooling water is known, the system volume (V) can be determined. The blowdown is resumed and the traced material concentration is measured as a function of time. The blowdown rate, and hence the holding time index, can be calculated from the decay of the tracer concentration as a function of time.

Time/cycle (*t*) One cycle is defined as the time required for water to make one trip around the circulating loop. This time is a function of the holding capacity and the recirculation rate.

$$t = V/R \tag{14.19}$$

Holding Time Index Holding time index (HTI) is defined as the time required for the concentration of any ion to dilute to 50% of its original concentration in a cooling tower. HTI is essentially the “half-life” of a chemical added to a system. HTI is calculated from the system volume (V), the blowdown rate (BD), and the natural logarithm of 2 (0.693) with Eq. (14.20).

$$\mathrm{HTI} = 0.693(V)/(\mathrm{BD}) \tag{14.20}$$

Unique Problems of Cooling Tower Systems

Open recirculating systems can experience unique issues that are not encountered in closed and once-through cooling systems. Some examples follow.

Ambient Air Effects Cooling towers scrub the air passing through them to provide the evaporative conditions, handling about 120 to 240 ft^3 of air per gallon of water (900–1800 m^3 of air per cubic meter of water). The atmospheric environment around a tower can have profound effects on the thermal performance of the cooling tower system.

In some areas, the air contains large amounts of dust, as in arid sections of the world, especially where dust storms are common. Cooling systems in areas prone to this problem cannot work effectively without side-stream filtration. In a complex industrial plant, solids may become airborne from dirt on roads, open areas between plant buildings, or from open storage of solids (e.g., ore, coal, lime, or limestone). Any of these sources of particulates is as damaging as silt and requires side-stream filtration. Lime and limestone dust can dramatically affect cooling water scale control programs.

A more subtle, difficult problem is the presence of acidic or alkaline gases in the atmosphere. These gases affect the pH of the system, a critical control factor in any chemical treatment program that has a direct bearing on the scale-forming or corrosive tendencies of the water. An unusual, but pertinent, example is an ammonia plant cooling tower located between the ammonia process and the nitric acid process. When the wind is from one direction, ammonia in the atmosphere raises the pH of the system water. When the wind is from the opposite direction, acidic nitrogen oxide gases reduce the pH. Although this is an exaggerated case, this example illustrates that the pH of the system may be affected by the air around the tower.

Another example of gas entry into a cooling tower is when rooftop cooling towers are located too close to boiler exhaust stacks. This can allow carbon dioxide, carbon monoxide, and sulfur gasses to be dissolved into the cooling water.

The most prominent of the atmospheric gases are acidic, and chief among them is carbon dioxide (CO_2), which occurs at an average concentration of about 0.03% by volume in the atmosphere. The amount of CO_2 supported in water at about 68°F (20°C) by this partial pressure is less than 1 mg/L. However, the actual CO_2 level in a cooling tower system varies considerably from one plant to another because of local atmospheric conditions, such as the presence of industrial stack gas discharges.

There is a definite relationship between CO_2, alkalinity, and pH (see Chap. 4 on Water Chemistry). Because CO_2 is variable, predicting the alkalinity concentration at a specific pH value is difficult.

If the atmospheric CO_2 concentration is constant, then the relationship between alkalinity and pH can be defined. The pH will vary as a logarithmic function of alkalinity. The pH will increase by the log of 2, or a value of 0.3, if the alkalinity doubles. Similarly, if the atmospheric CO_2 doubles with a fixed alkalinity, the pH will be reduced by the log of 2 or 0.3 pH units. The expected equilibrium pH of any new system can only be established empirically, unless there is a record of previous experience near the new cooling tower or strong evidence that the average atmospheric CO_2 concentration is constant.

Fill Fouling Cooling towers are sometimes built with high-efficiency film fill instead of splash fill. High-efficiency fill provides greater cooling capacity with less volume, because water passages are closely packed together (Fig. 14.28). High-efficiency fill is much more prone to fouling with suspended solids and microbial contamination than splash fill (Fig. 14.29).

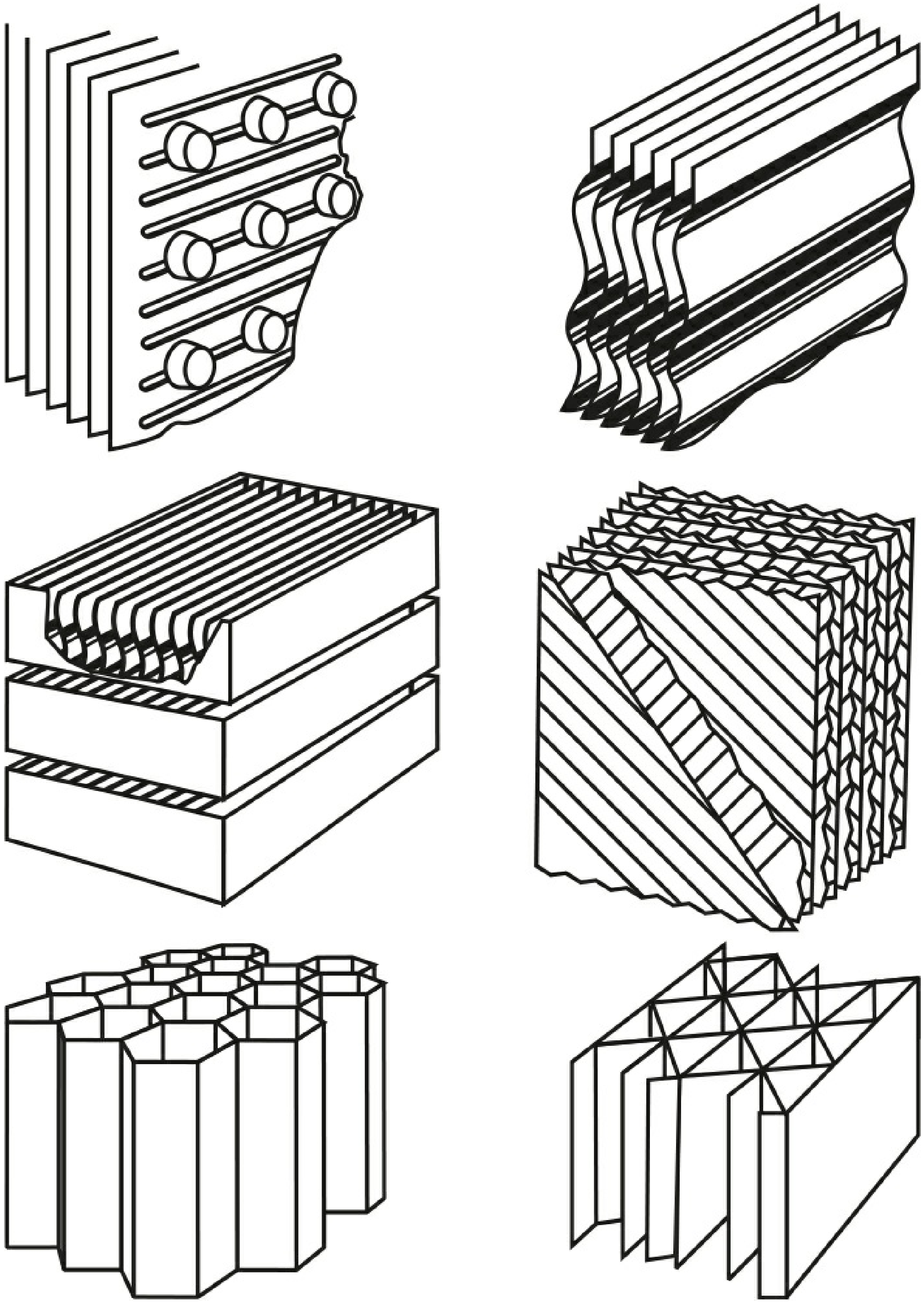

FIGURE 14.28 Diagram of several types of film fill, showing the variation in size of the passages for water and air.

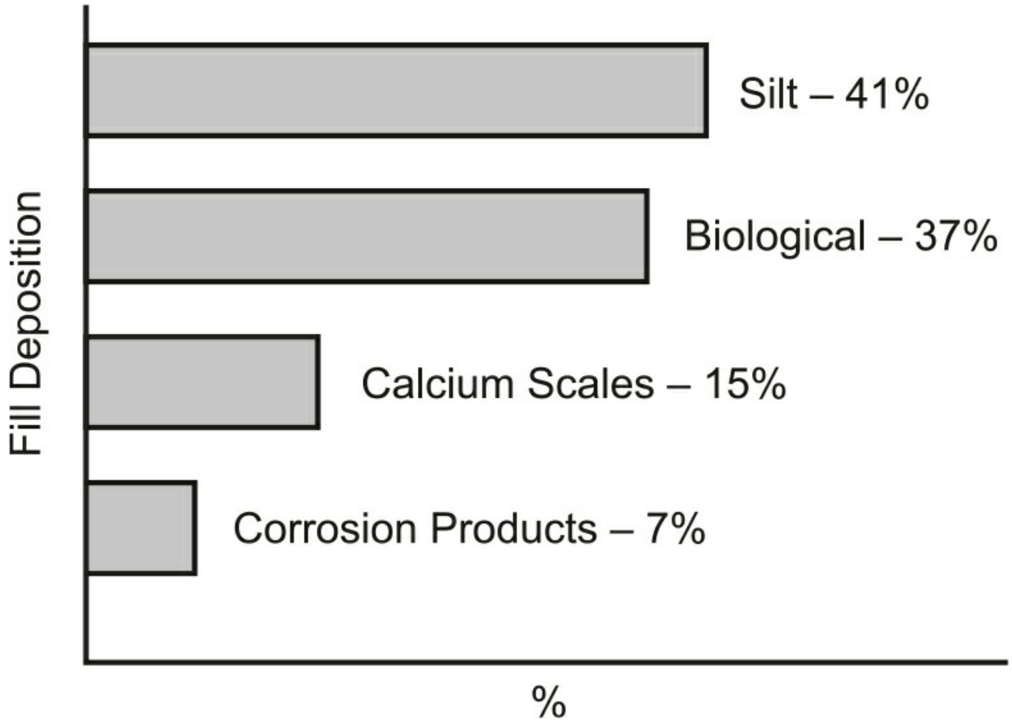

FIGURE 14.29 Average breakdown of cause of cooling tower fill deposits.

When fill fouling occurs, the fouling may be seen at the ends of the fill where water enters or leaves the fill. In some cases, scaling from hardness and alkalinity can cause severe fouling, as shown in Fig. 14.30. However, this is not always the case. High-efficiency fill is often prone to deposition about one-third of the way down from the top of the fill surface. This will be difficult to find, especially since there may be no evidence looking from the top or the bottom of the packing. Depending on the type of foulant on the fill, the material will range from white to brown or black. Scale deposits are generally white and may be either a continuous coating or spotty deposits that occur in wet-dry areas. Microbial deposits will vary in color depending on the organism. Suspended solids will often be gray or brown deposits.

FIGURE 14.30 Heavy fouling of film fill caused by inorganic scale formation.

Icing In some climates, either in the extreme northern or southern areas of the world, ice can form in any of the water-wetted areas of the cooling tower. This may occur particularly near the outside inlet for the cold air. The weight of ice on cooling tower components can cause significant damage. Icing on air intake louvers and packing next to louvers can restrict airflow or cause structural damage due to the weight of ice accumulation.

Wood Degradation Most tower lumber is either preservative treated or a rot-resistant species. Plastic components are often used in place of wood in newer towers. However, some towers have been constructed of cheaper, spruce wood, which has less natural resistance to biological attack. Wood can exhibit a variety of forms of attack in water-wetted systems:

1. Chemical surface attack or delignification is due to the selective removal of lignin from wood. Excessive chlorination at elevated pH for prolonged periods may cause this attack. Chemical surface attack is most prevalent in the flooded wood components or frequently wetted areas. Chemical attack is a thin-layer surface attack and can be detected and controlled, if the attack is discovered before serious damage occurs. This form of surface attack is virtually nonexistent in the pH range of 6 to 8.
2. Iron rot is a chemical attack caused by the formation of iron salts around corroding ferrous parts in contact with wood. The wood in the adjacent zone has a charred appearance and may be more susceptible to fungal attack. Since connections are affected in many cases, extensive repairs may be required.
3. Biological surface attack (soft rot) is caused by fungi, which selectively attack cellulose of damp wood, leaving behind the lignin. This attack is characterized by a dark appearance, and the wood surface becomes soft and spongy or checked.
4. Biological internal attack occurs below the surface of the wood, and often goes undetected until the infection has spread widely, resulting in serious structural damage. The decay can be white rot, attacking both cellulose and lignin and leaving a spongy or stringy mass, or a brown rot, attacking primarily cellulose and leaving a brown cube-like pattern. This type of attack is more apt to occur in the warm, moist, but non-flooded portions of the tower.

The types of organisms that cause biological attack are covered in Chap. 17 on Cooling Water Biology.

Basin Sludge The presence of sludge in the cooling tower basin can cause problems throughout the cooling system. Basin sludge can be a source of microbial slime problems elsewhere in the cooling system, especially heat exchangers. Basin sludge can also harbor hazardous Legionella bacteria that can reinoculate the tower water if released from the sludge. (See Chap. 20 on Legionella and Legionellosis.) If the source of the sludge is either windblown dust and debris, or suspended solids in the makeup water, the cost of cleaning and additional dispersant may possibly help to justify the cost of side-stream filtration equipment. Often, a chlorination feed system that sweeps the total basin will have a beneficial effect on microbial control in the total system and help to minimize problems from sludge in the basin.

Intermittent Operations Some equipment, such as a chilled water system, often operates on a seasonal basis. Any system that is out of service can be a site of microbial growth. Stagnant water can also create severe corrosion problems. An out-of-service system should be monitored for microbial activity and inhibitor concentration maintained at proper levels. Periodic circulation is recommended.

Water Recycle Recycle or reuse of wastewater in cooling tower systems can offer economic and environmental benefits. These benefits generally come with added cost or risk to the system operation. Treatment programs may require modification to maintain low corrosion rates and clean heat transfer surfaces with the recycled water. Cooling tower systems are often considered the best candidate for use of recycled water, because of relatively lower water quality requirements and high usage rates. Even so, many potential problems exist. Increased dissolved solids in the wastewater can increase scaling or corrosion potentials. Organic contaminants in refinery and chemical plant wastewaters can cause fouling of system surfaces and increase microbial growth. Nutrient materials such as phosphate and ammonia can increase microbial growth. Depending on how the wastewater will be used, these contaminants must be removed or treatment programs modified to deal with these effects.

CHAPTER 15

Cooling Water Deposition

Water is used in cooling systems because it is widely available in most industrial areas, is easy to handle, and has a high capacity to carry heat away from processes. Water is often called the universal solvent—a property that can cause unwanted side effects for industrial applications. Water can dissolve many substances. As a result, water can cause corrosion of metals used in cooling systems. Dissolved ions in the water may exceed the solubility of some minerals and cause scale formation. The life-giving properties of water can encourage bacterial growth that can foul system surfaces. Suspended solids in the water may deposit in low-flow areas and create unwanted fouling. These four problems (corrosion, scale, fouling, and microbial growth) require proper treatment and control to maintain the integrity and reliability of a cooling system.

For many years, Nalco has described the interrelated nature of these four cooling water problems in terms of a triangle (Fig. 15.1). The problems of corrosion, scale, fouling, and microbial growth do not happen in isolation. These problems can occur simultaneously, and each one can influence or even cause the other problems. The interrelated nature of the four problems is very important to understanding and controlling cooling system performance. A treatment program cannot address only one or two parts of the triangle, because another untreated issue can quickly cause any of the other problems. This is particularly true of biofouling, which can directly and indirectly cause corrosion, scale formation, and fouling by suspended material. Biofouling is at the center of the triangle because biological organisms can rapidly get out of control and swiftly increase the rate of any of the other three problems. The triangle is also a reminder that one of the central aspects of a good treatment program is effective microbial control. From a practical point of view, the four problems cannot be viewed individually, but must be addressed together in a complete program including proper treatment, system management, system control, and results monitoring.

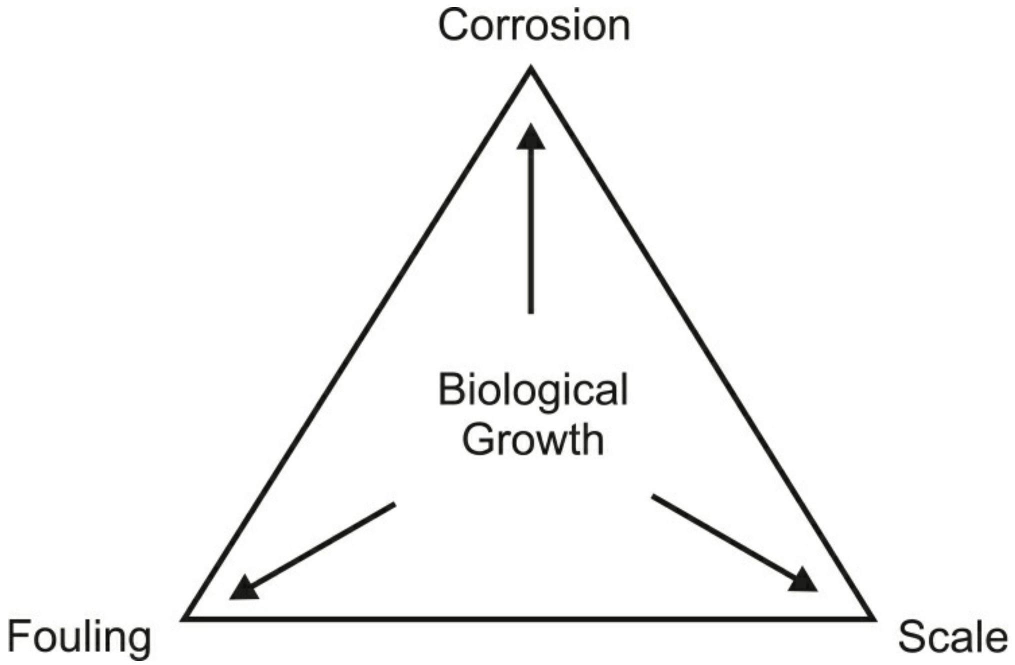

FIGURE 15.1 The problems in cooling water systems are closely interrelated, with biological growth as the central problem that can cause corrosion, scale, and fouling to occur or increase.

The need to look at all of the problems to identify the root cause can be illustrated by a simple case history. Exchanger performance monitoring showed that fouling was occurring in a cooling water system. This fouling reduced exchanger heat transfer efficiency and reduced overall system performance. A dispersant was added to the treatment program; however, the deposition continued. An analysis of the deposit was then obtained, showing that the fouling was mostly iron oxide from corrosion of the system. The corrosion inhibitor dosage was increased, along with the dispersant, but the fouling problem did not stop. A complete survey of the system showed that microbial growth was not effectively controlled and anaerobic corrosive bacteria were present in the system. These bacteria can directly influence corrosion rates in a cooling system. Improving oxidizing biocide control along with biodispersants to control the microbial problems in the system, reduced system corrosion and hence the iron fouling. This illustrates that biological growth is often the central problem in cooling water systems.

Even though the problems in cooling systems are interrelated, separate discussion and understanding of each of the four problems is necessary to obtain best results for cooling water system control. All treatment programs are made of individual components that address aspects of each problem. An understanding of the individual components is necessary to understand how the treatment programs function, and to select the correct program. Therefore, this section provides a basic understanding of corrosion, scale, fouling, and biological growth that occur in cooling water systems. Only in this manner can the best solution be chosen for complete treatment in any individual system.

Cooling system operation directly affects reliability, efficiency, and cost of any industrial, institutional, or power industry process. Maintaining control of corrosion, deposition, microbial growth, and system operation is essential to provide the optimum total cost of operation (TCO), as described in Chap. 14 on Cooling System Dynamics. Using computer optimization to select both an appropriate treatment program and optimum operating conditions to minimize system stresses is the first step. The next step is implementation of an appropriate monitoring program to evaluate system conditions and treatment program performance. The final step is the use of superior monitoring and control technology to control system stress, optimize operating conditions, and control program parameters to minimize TCO.

Consequences of Deposition

Scaling and fouling can be separate processes but are often considered the same problem. The terminology is such that both words can be used to describe similar or separate aspects of deposition. In this book, deposition is considered the overall process that includes scaling and fouling. Scaling is a chemical process involving precipitation of insoluble compounds, whereas fouling is predominantly a physical process involving the settling of suspended particles. Scaling and fouling are related because each problem can aggravate the other. The two processes are described separately, but scaling and fouling generally happen together, and a complete treatment program must address both problems.

As deposits grow, water flow rate decreases and pumping backpressure increases. The deposits have lower thermal conductivity than the metal heat exchange surfaces, causing reduced heat transfer. Deposition results in decreased plant efficiency, reduced productivity, schedule delays, increased energy costs, loss of production from downtime for maintenance, and increased costs for equipment repair and replacement. All of these effects directly lead to higher operating costs and decreased profitability. Deposition also has a capital cost penalty, because heat exchangers are commonly built about 15% larger to accommodate the normal fouling that will occur.

Common types of deposition in cooling systems are:

- Mineral scale—precipitation of insoluble compounds from ions in the water
- Suspended material—insoluble material that can settle in low flow areas
- Corrosion products—deposits that result from insoluble materials formed by corrosion
- Process leaks—typically organic foulants introduced from the process being cooled
- Microbial deposits—created by the action or growth of microorganisms

The component elements of a deposit are typically determined by X-ray fluorescence (XRF). This technique identifies the elements present by measuring the characteristic X-rays released by an element, when the sample is irradiated by an X-ray source. The compounds that may be present in the deposit are determined by X-ray diffraction (XRD). The sample is irradiated with an X-ray beam, and the diffraction pattern that results is analyzed. Crystalline materials produce a diffraction pattern that is unique for each mineral present. XRD can differentiate between crystalline and amorphous (noncrystalline) deposits, but cannot identify the composition of amorphous materials.

Table 15.1 shows examples of deposit analyses containing typical cooling system deposits from a variety of locations in different cooling tower systems. Deposits of primarily calcium carbonate are common and can be found in various areas of the system (Samples 2, 3, and 4). Calcium sulfate is less common, but can be found in the tower fill or heat exchangers, depending on the form of calcium sulfate that occurs (Sample 1). Iron oxide is found most often in system piping and exchangers but may be transported through the system to the deck of a cooling tower (Sample 5). Sample 6 is an example of organic fouling that may have come from a process leak.

Sample Number	**1**	**2**	**3**	**4**	**5**	**6**
Source of Deposit	**Tower Fill #1**	**Heat Exchanger**	**Tower Fill #2**	**Tower Basin**	**Tower Deck**	**Cooling Tower**
XRF Elemental Analysis*						
Aluminum as Al_2O_3				1%		
Copper as CuO					1%	2%
Calcium as CaO	30%	49%	49%	45%	1%	1%
Iron as Fe_2O_3		2%		1%	86%	
Fluoride as F		1%				
Magnesium as MgO	1%	2%	1%	1%	1%	
Manganese as MnO_2					1%	
Phosphorus as P_2O_5	1%	5%	1%	1%	2%	1%
Silicon as SiO_2	9%	2%	2%	9%	3%	
Sulfur as SO_3	38%	1%	2%	1%		
Zinc as ZnO	4%			1%	1%	
Loss at 925°C†	17%	38%	45%	40%	4%	96%
Total	100%	100%	100%	100%	100%	100%

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*The results for the X-ray fluorescence (XRF) analysis were normalized to loss at 925°C, such that XRF + L925 = 100%.

†The loss at 925°C includes water of hydration, CH_2Cl_2 extractables, all organics (carbon, hydrogen, nitrogen), many sulfur compounds, the CO_2 from most carbonates, and some volatile compounds.

Sample Number	**1**	**2**	**3**	**4**	**5**	**6**
Source of Deposit	**Tower Fill #1**	**Heat Exchanger**	**Tower Fill #2**	**Tower Basin**	**Tower Deck**	**Cooling Tower**
Other Analyses						
CH_2CH_2 extractible	Not detected	Not detected	Not detected	<1%	Not detected	65%
Carbonate as CO_2	4%	33%	36%	30%	Not detected	Not detected
Most Probable Composition	Calcium sulfate	Calcium carbonate	Calcium carbonate	Calcium carbonate	Iron oxide	Organic matter
	Calcium carbonate	Calcium phosphate		Silica		Spot test indicates bacteria
	Silica					

TABLE 15.1 Analyses of Cooling System Deposits That Contain Mineral Scale, Suspended Solids, Corrosion Products, and Organic Foulants

Scale is one of the most common problems encountered in cooling water systems. Scale is the precipitation of minerals resulting when the concentration of ions in solution exceeds the mineral solubility. Scale generally forms hard and adherent layers, which retards heat transfer. Scale in transfer pipes can reduce water throughput, which can accelerate fouling further. Scale formation generally needs a temperature gradient, but can occur without a temperature differential in some conditions. Scale can also form in the cooling tower fill, where the ions in the water concentrate by evaporation.

Fouling is distinguished from scaling in that fouling deposits are formed from material suspended in water. Fouling is the aggregation of insoluble material through physical processes. Materials that cause fouling include suspended solids, organic contaminants like oil, corrosion products, and microbial growth. The combination of these problems complicates the fouling mechanism and is the reason that fouling is difficult to prevent. Fouling can occur without a temperature difference in any part of a cooling system, including cooling tower deck, basins, and fill.

In general, deposition will occur due to variation of environmental factors such as an increase of suspended solids in the makeup water, lack of control of cooling system parameters such as concentration ratio, or due to misapplication of treatment programs. This chapter will cover the scale formation process and fouling from insoluble material. Examples of common deposits found in cooling water systems will be covered. Microbial fouling will be covered in a separate chapter.

The Scale Formation Process

Scale forms when crystals of an insoluble mineral grow on surfaces in cooling systems. In some cases, precipitation can occur in the bulk solution, and scale then forms by an agglomeration of suspended scale particles, which deposit on surfaces in a fouling process. Scale can be crystalline or amorphous in nature. Amorphous refers to the lack of an ordered or crystalline structure. Understanding the conditions for scale formation and which factors affect the solubility of a mineral, will help to understand how to control this part of the deposition process.

For scale to occur, the right conditions for scale formation must exist. These conditions include:

- Saturation of the component ions of the mineral
- Nucleation sites—for example, rough metal surfaces or small particles of scale
- Contact time to allow the growth of scale crystals
- Scale formation rate exceeding the dissolution rate
- Strength and hardness of the scale is sufficient to resist the shear forces of flowing water

Scale formation may occur when ions of a given mineral in the cooling water concentrate above the solubility of that mineral. Scale can form anywhere in the system in combination with corrosion, fouling by suspended material, or with biofouling. The presence of suspended solids, corrosion products, corrosion sites, welds, crevices, surface roughness, oxide films, and evaporation over the tower fill can initiate seed scaling.

Solubility Is an Equilibrium Process

Generally, minerals that can precipitate in cooling systems are ionic solids. When a solid dissolves in water, the ions that form the compound are released into solution. Even when sparingly soluble minerals like calcium carbonate ($CaCO_3$) are added to distilled water, the mineral will dissolve as shown in Eq. (15.1):

$$CaCO_3 \rightarrow Ca^{+2} + CO_3^{-2} \tag{15.1}$$

When the salt is first added, the ions dissolve rapidly. As more salt is added, the concentrations of the ions soon become large enough that the reverse reaction (precipitation) starts to compete with dissolution. Eventually, the calcium (Ca^{+2}) and carbonate (CO_3^{-2}) ion concentrations become large enough in the solution that the rate of precipitation equals the rate at which $CaCO_3$ dissolves. Once that happens, there is no net change in the concentration of these ions with time, and the reaction is at equilibrium. When the system reaches equilibrium, the solution is called a saturated solution, because the liquid contains the maximum concentration of ions that can exist in equilibrium with the solid salt. The equilibrium is represented in Eq. (15.2):

$$CaCO_3 \rightleftharpoons Ca^{+2} + CO_3^{-2} \tag{15.2}$$

The amount of salt that must be added to a given volume of solvent to form a saturated solution is the solubility limit of the salt, and defines the saturation ratio (SR) or saturation index (SI) at a given set of conditions (temperature, pH, ionic strength, etc.). At equilibrium, the SR or SI equals 1.0. A supersaturated solution exists when the concentration of the ions is higher than the equilibrium levels ($SR > 1$). In this case, the rate of precipitation may increase. If the concentration of ions drops below the equilibrium levels ($SR < 1$), solubility increases, and precipitation will stop. A cooling tower system can reach $CaCO_3$ saturation very quickly. When the conditions of water chemistry, pH, and temperature exceed the solubility limit, $CaCO_3$ precipitation can occur.

Nucleation and Scale Formation

In a cooling water system, scale can appear rapidly, and grow to visible thick layers in a short time. Although the growth of scale can seem very simple, the process of scale formation is a series of steps as illustrated in Fig. 15.2. First, water with dissolved minerals must be concentrated so that the ions of a given mineral are above the solubility of that mineral (supersaturation). Crystallization of scale will only occur if some degree of supersaturation exists. The degree of supersaturation is a prime factor for controlling the deposition process. Once supersaturated, there is typically an induction period before nucleation occurs. The induction period is defined, as the time required from the point of supersaturation to the initial formation of small particles of mineral scale.

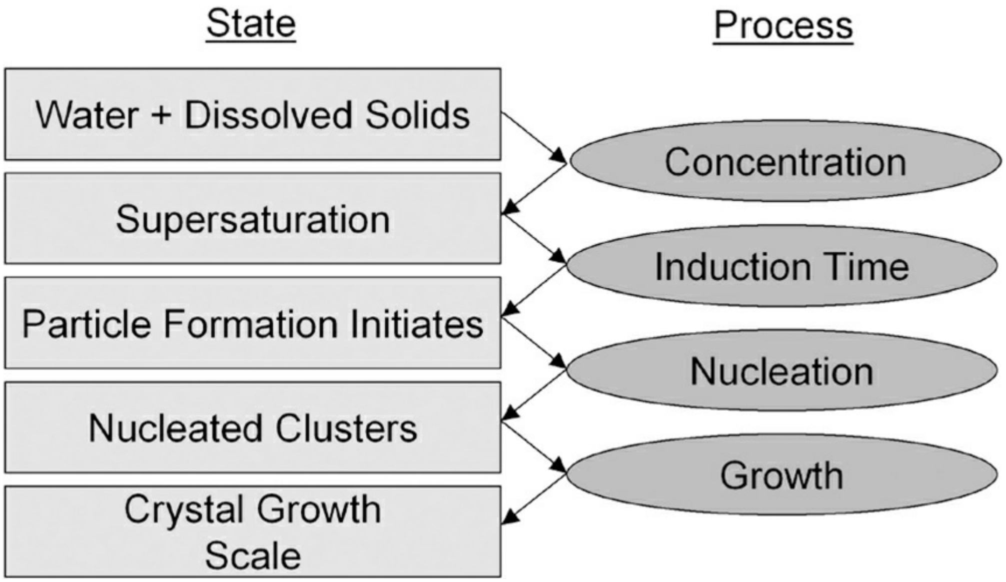


FIGURE 15.2 The steps that lead to scale formation.

A supersaturated solution will not form scale unless some solid sites exist where crystals can grow. These sites may be seed crystals of the mineral, suspended solids particles, rough metal surfaces, or microbial deposits. The formation of many small particles that act as sites for additional crystal growth is called nucleation. This nucleation process can follow two different paths, either occurring spontaneously or induced by external forces.

Homogeneous versus Heterogeneous Nucleation

Nucleation occurs by two basic mechanisms: homogeneous and heterogeneous nucleation. Homogeneous nucleation occurs spontaneously (self-seeding) and can be caused by a high degree of supersaturation of the scaling ions. Heterogeneous nucleation occurs when foreign particles or irregularities on system surfaces seed scale formation. Heterogeneous nucleation is more common in cooling water systems, due to the presence of suspended solids, microbial deposits, corrosion products, corrosion sites, welds, crevices, surface roughness, and oxide films, all of which can initiate nucleation or seed the formation of scale.

For homogeneous nucleation to occur, a minimum number of molecules (in the thousands) must orient themselves into a fixed lattice. If nuclei are too small, these nuclei will redissolve. The nuclei become stable after exceeding a certain size (above a critical radius). The time required for nucleation varies, depending largely on the degree of supersaturation. The time required for nucleation decreases as supersaturation increases.

In reality, homogeneous nucleation is a difficult process. The molecules in solution must collide, not redissolve, orient themselves into a fixed crystal lattice, and additional molecules must add to the surface to continue the scale formation process. Many of these initial clusters of scale molecules must be present to form a noticeable amount of scale. The solution must remain supersaturated so that the process continues.

When nucleation begins, several processes are possible:

- The nucleated particles can redissolve, if the level of supersaturation is not sufficiently high or if an inhibitor is present.
- The nucleated clusters can form on solid surfaces in the system and grow into layers of scale.
- The nucleated clusters can form in the bulk solution, if the level of supersaturation is very high.
- If nucleated clusters form in solution, the process of agglomeration to form scale may be balanced by dispersion to keep the particles separated and floating in the water.

The formation of stable nucleated clusters depends on the free energy of the molecules in solution, compared to the free energy released when the solid is formed. Homogeneous nucleation first requires energy to bring the molecules together. The energy required is related to the degree of supersaturation, such that a highly supersaturated solution requires less energy for spontaneous nucleation. Energy is required to form nucleated clusters up to a certain critical radius (Fig. 15.3). Above this critical particle size, energy is released by the formation of the solid. As crystal growth continues, the free energy released by the solid is greater than that required to form the nucleated clusters, and scaling continues.[1]

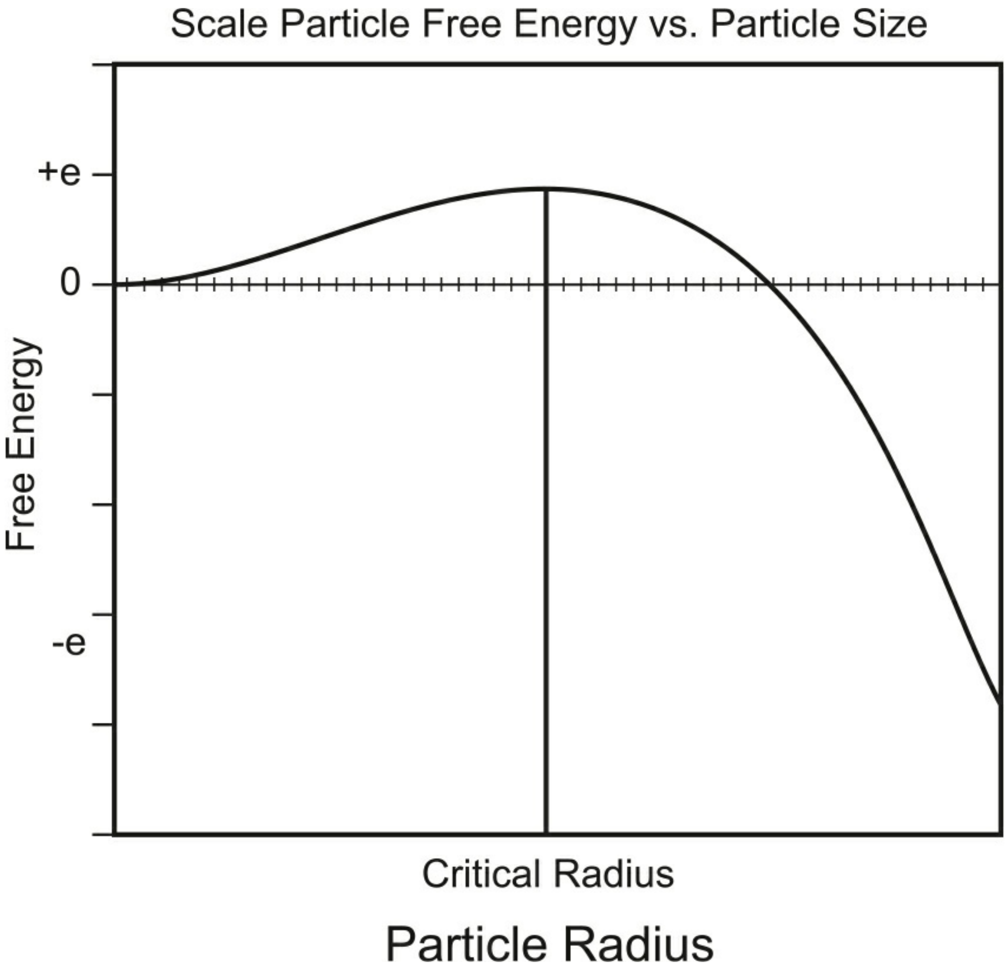


FIGURE 15.3 The behavior of new nucleated clusters depends on the particle size. The nucleated cluster can grow or dissolve, whichever results in a decrease of free energy of the system.

In heterogeneous nucleation, the presence of impurities or foreign material in solution can significantly affect the rate of nucleation. Inhibitors can slow the scale formation process. Suspended solids, microbial growth, corrosion products on surfaces, and rough metal surfaces in cooling systems, can increase the formation of nucleated clusters of scaling minerals. These impurities stimulate the scale formation process by reducing the energy required to form the nucleated clusters of scale molecules, or reduce the level of supersaturation needed to start the nucleating process. The free energy change of formation of the crystal nuclei by heterogeneous nucleation is lower than the energy change required for homogeneous nucleation.

At this point, the scaling process can go either way, because the growth of scale depends on the size of the particles and energy of the system. If the energy is not sufficient to reach the critical size, the nucleated clusters will redissolve. If enough energy is present, the nucleated clusters will reach the critical size, continue to grow, and scale will form. One role of scale inhibitors can be explained during this nucleation process. The inhibitor can be adsorbed onto growing nucleated clusters and prevent them from reaching the critical size. The nucleated clusters will then redissolve and release the inhibitor back into solution. In well-inhibited and controlled systems, this illustrates why the inhibitor is not consumed while preventing scale formation. However, if the system is not controlled properly, the nucleated cluster will continue to grow past the critical size. These growing scale clusters will consume any adsorbed scale inhibitor. Monitoring this process of inhibitor consumption can be used to measure scaling stress in a cooling system. This is covered in more detail in Chap. 19 on cooling water treatment and control.

Crystal Formation

This is the beginning of a fixed crystal lattice. The lattice may form layers that allow growth to continue by adding individual scale molecules. The continued growth into crystalline scale is dependent on a variety of factors:

- Degree of supersaturation
- Temperature
- pH of the water
- Presence of impurities or seed crystals
- Concentration of dissolved carbon dioxide (CO_2) will affect nucleation of calcium carbonate
- Flow velocity of the water

Once nucleation has formed stable particles, larger than the critical size, visible scale crystals will grow. These growing crystals generally spread outward in a layer (called a terrace) as shown in Fig. 15.4. Each layer is only one molecule thick, and may have other seed clusters growing on top of the layer (forming steps). If solution conditions are right, the growth will continue as new molecules continually adsorb onto the growing steps or form new clusters. Scale inhibitors can affect either the formation of the initial molecule clusters or the growing crystal steps.

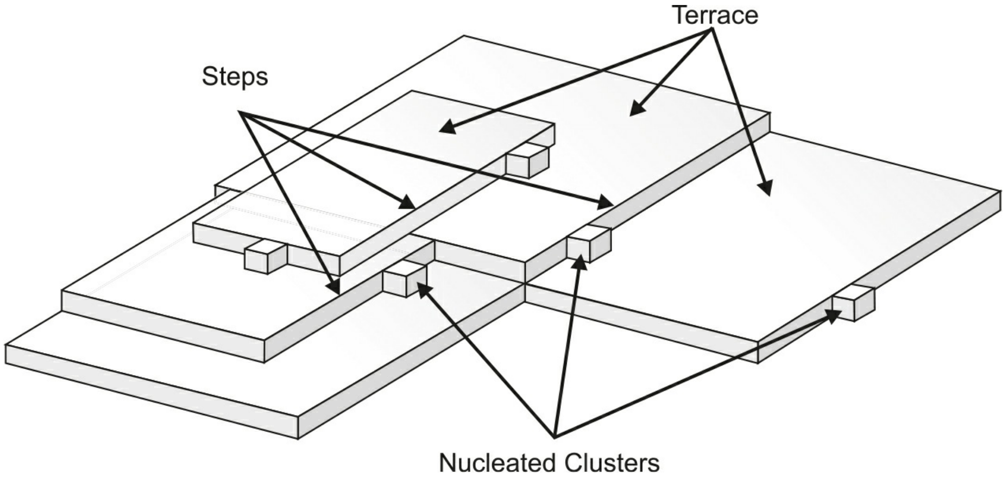


FIGURE 15.4 Crystal growth occurs in layers with new crystals forming along the edges of each terrace.

Crystals have distinct configurations, in which individual molecules are oriented into precise crystal structures. The specific form of crystal that grows, depends on the solution conditions and rate of scale formation. If precipitation is rapid, the scale molecules may simply adsorb in any orientation, forming an amorphous deposit. Impurities may adsorb onto the scale surface, which changes the direction of the growing layer. Whether the crystals grow in a defined lattice, in misaligned layers, or in an amorphous mass, depends on the type of mineral, its properties, the supersaturation level, pH, temperature, impurities in the solution, and the presence of scale inhibitors.

Kinetic versus Thermodynamic Factors

The solution will try to maintain the lowest energy, whenever possible. The precipitation of a solid scale may be a lower energy state, than having the same ions dissolved in the solution. This is the thermodynamic consideration of scaling. On the other hand, some minerals take a very long time to form, even if the energy of the solid scale is less than that of the solution. The rate of formation is the kinetic aspect of scale formation. The difference between the thermodynamic and kinetic factors can be seen in the following simple example. Quartz has a much lower solubility than amorphous silica, but the rate of formation of quartz is so slow that quartz will not occur in a cooling system. This may not seem important to the operator who has silica scale in a tower, but this difference is essential to the understanding and inhibition of any mineral scale. With this knowledge, system conditions can be controlled to minimize the energy driving forces for precipitation, and inhibitors can affect the kinetic rate of scale formation and growth.

Phase Transitions

Scale that precipitates rapidly often forms a relatively porous structure that is easily removed with little mechanical effort. However, aging can change the physical characteristics of most scale deposits. Scale tends to harden and becomes more dense during aging. Older scale deposits are more adherent and difficult to remove. The aging phenomenon is due to dissolution, redeposition, and regrowth of crystals, or to phase changes involving hydration or dehydration. These aging processes can cause the individual crystals to become a solid, unified mass. Aging of scale is accelerated on heat transfer surfaces.

Adherence

A primary factor influencing scale adherence is surface roughness. Consequently, adherent scale forms more readily on corroding surfaces than on noncorroding surfaces. In addition, corrosion by-products tend to mix with forming scales and thereby increase adhesion of the mixture. Easily corroded metals result in significantly more deposits (mixtures of scale and corrosion products) than metals that do not corrode. When an alloyed metal surface is very smooth, scale deposition is lower than on a rough surface. Thus, microscopic surface roughness, whether naturally present or produced by corrosion, tends to increase the adherence of scale deposits.

Factors Affecting Scale Formation

Cooling water chemistry, operating parameters, and basic system design factors affect scale formation. These include but are not limited to the following:

- Concentration—The buildup of sparingly soluble compounds due to evaporation by a cooling tower.
- pH shifts—Stripping of CO_2 from carbonate buffered water causes the pH to increase.
- Process leakage—Can cause fouling and increase pH, making many scale-forming minerals less soluble.
- Temperature—The skin temperature of heat transfer surfaces can significantly affect scale formation of some minerals.
- Corrosion control—Cathodic corrosion inhibitors like phosphate or zinc can contribute to scaling when misapplied. This can result in precipitation of calcium phosphate or zinc compounds.
- Water quality—The presence of microbial growth or suspended solids in the water can increase deposition potential.
- Operational variability—Poor control of cooling tower water concentration ratio, changes in makeup water composition, and poor control of inhibitor dosage can result in scale formation.
- Misapplication of inhibitor programs—Over dosage of some inhibitors can cause scale.

Solubility factors affect the equilibrium process and the potential for scale formation. Any mineral in solution is affected by the total composition and conditions of the solution. Some of the factors that influence scale formation should be understood in more depth.

Common Ion Effect

The concentrations of ions in solution are affected by all equilibria and all ions present in the solution. The simplest and most significant effect is called the common ion effect, which occurs when an ion comes from two different salts in solution. For example, if sodium carbonate (Na_2CO_3) is added to water saturated in $CaCO_3$, the increased concentration of CO_3^{-2} will shift the equilibrium to cause $CaCO_3$ precipitation.

The Role of Temperature

Most compounds are more soluble in water as temperature increases. This is called normal or direct solubility. Scaling materials such as gypsum ($CaSO_4 \cdot 2H_2O$) and silica (SiO_2) have normal solubility. Under conditions of supersaturation, these materials may selectively form scale in cooler parts of a system, such as tower basins or fill. However, many of the common scale-forming minerals have inverse temperature solubility, which means that the solubility of these minerals decreases with an increase in temperature (Fig. 15.5). Calcium carbonate and calcium phosphate are inversely soluble and precipitate where temperature is highest. Thus, high skin temperature can lead to localized scaling of the heat exchanger surfaces, which reduces heat transfer.

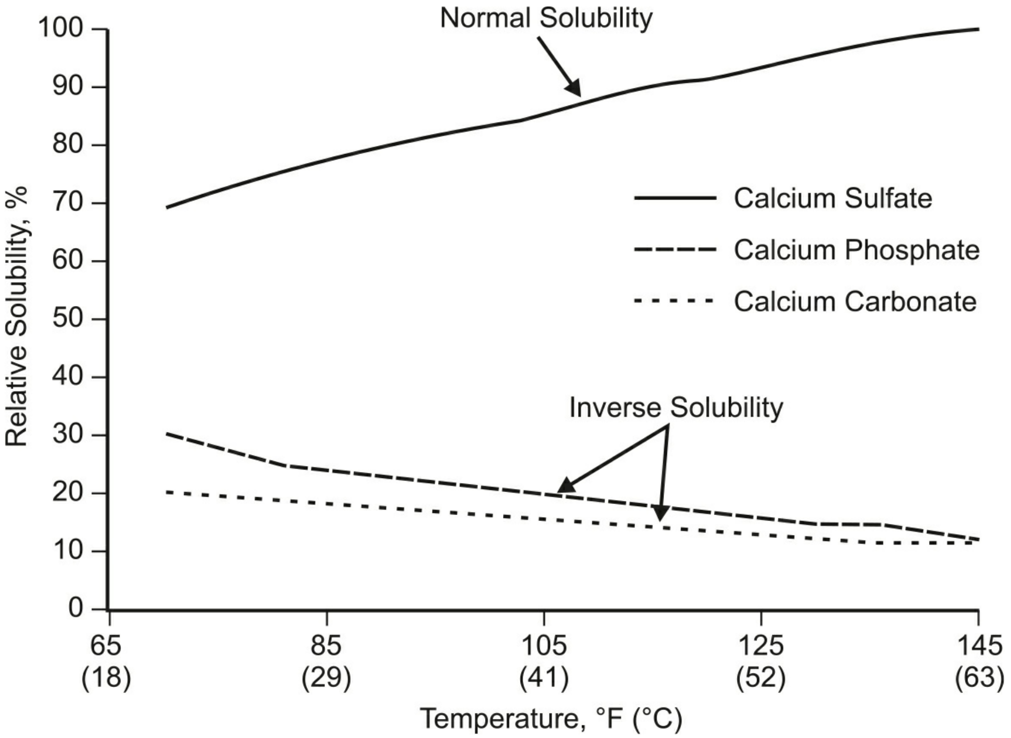


FIGURE 15.5 Example of how temperature affects the solubility of directly and inversely soluble compounds.

As a result, the solubility of potential scaling minerals will be different in different parts of the system (Fig. 15.6). Scale control is important throughout the entire system. Deposition can reduce the efficiency of either the heat transfer process in exchangers, or water and air flow in the cooling tower. Either effect can have a negative impact on process efficiency.

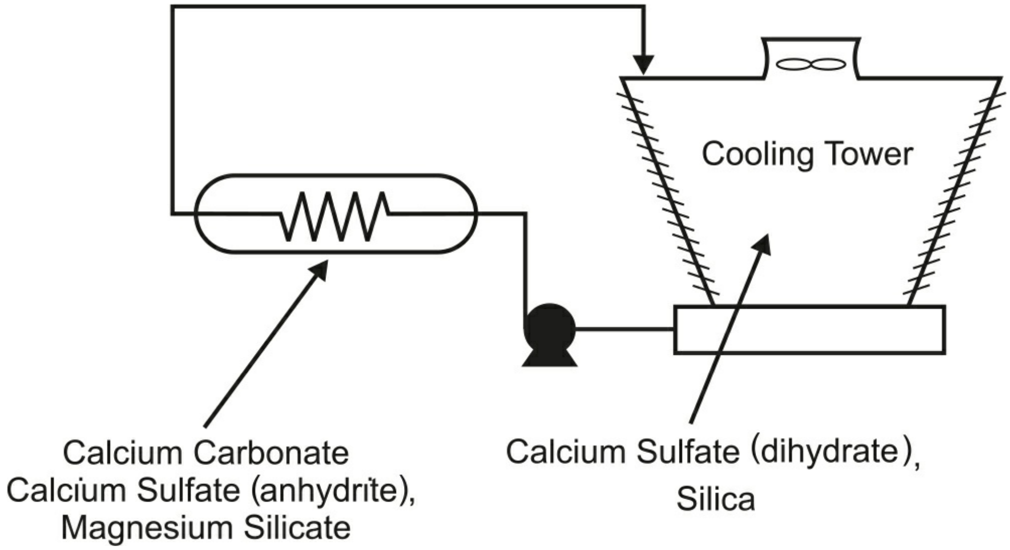


FIGURE 15.6 Minerals that are insoluble at high temperature (inversely soluble) may precipitate in heat exchangers, while minerals that are insoluble at low temperature (directly soluble) may precipitate in the cooling tower fill.

Ionic Strength and Particulate Material

High total dissolved solids (TDS) caused by ions that do not precipitate (e.g., sodium, potassium, and chloride) can extend the solubility of some scaling salts such as calcium sulfate ($CaSO_4$). Systems that have high TDS will benefit most from this effect (Fig. 15.7). On the other hand, high suspended solids increase scale potential primarily by increasing the number of nucleation sites where scale crystals can form.

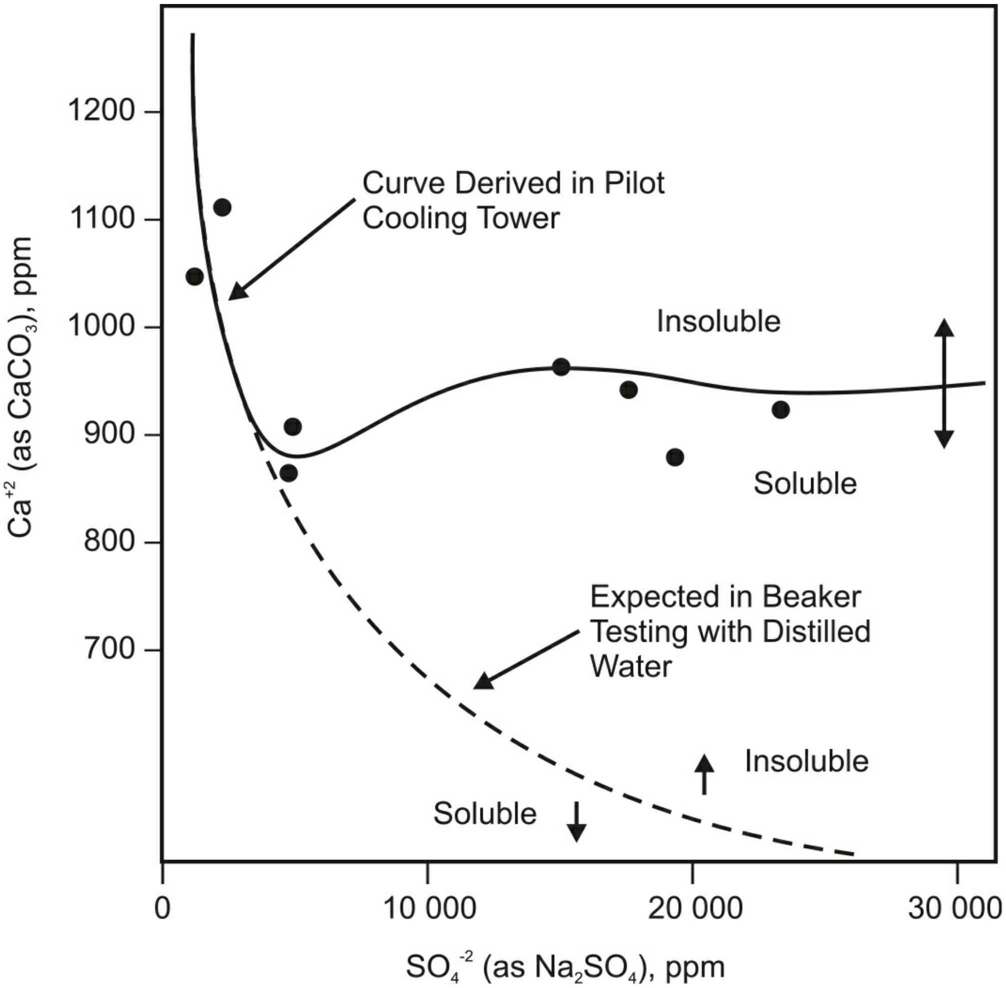


FIGURE 15.7 Example of how high conductivity can increase solubility of a scaling mineral like calcium sulfate.

Ion Pairing

Certain ions form a soluble ion pair that will decrease the deposition potential of other scale-forming salts. For example, $CaCO_3$ will have a given solubility by itself in water. When magnesium chloride ($MgCl_2$) is added, the solubility of Ca^{+2} is increased, due to the formation of more soluble magnesium carbonate ($MgCO_3$) and magnesium bicarbonate ($Mg(HCO_3)_2$) ion pairs in solution. The ion pair is a weak association of the two ions, but this pairing can have a positive effect (Fig. 15.8). This effect is the opposite of the common ion effect mentioned earlier.

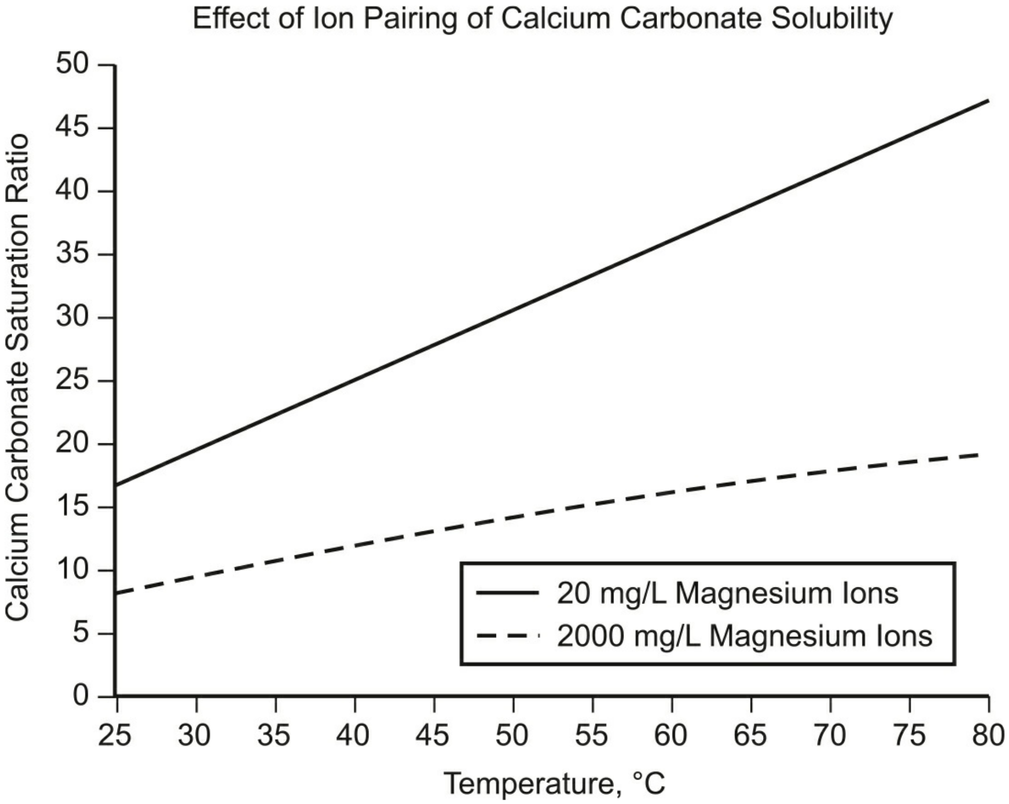


FIGURE 15.8 Illustration of how magnesium carbonate ion pairs can increase calcium carbonate solubility.

Effect of System pH

System pH has a significant effect on scale deposition in cooling water systems. As pH increases, so does the scaling potential for most common scales in cooling water, including calcium carbonate, calcium and zinc phosphates, zinc hydroxide, and magnesium silicate. Low pH excursions accelerate corrosion, thereby producing soluble corrosion products, which can directly or indirectly promote scale formation.

In cooling towers, the contact between air and water in the tower will strip CO_2 from carbonate buffered water, causing the pH to increase. This also changes the balance of bicarbonate (HCO_3^-) and carbonate (CO_3^{-2}) alkalinity. If concentration ratio and pH are not controlled, this shift in alkalinity caused by the stripping of CO_2 can lead to scale formation.

Flow Velocity and Hydrodynamics

Low water flow velocity [< 2 ft/s (0.6 m/s)] in heat exchanger tubes can result in nonturbulent or laminar flow. This creates a very low velocity boundary layer of water next to the metal surface. This phenomenon results in less efficient convective heat transfer and produces higher surface temperatures. The extent of scale formation depends on the steady-state balance between scale-forming processes such as surface precipitation or particle agglomeration, and scale removal processes such as removal by shearing or sloughing. The rate of removal by flow shear directly depends on flow velocity.

Coprecipitation

Coprecipitation is the capture of an ordinarily soluble mineral with a scale that is precipitating. An example is the precipitation of silica with calcium carbonate, magnesium hydroxide, zinc hydroxide, or ferric hydroxide, when silica is present below the level at which precipitation of SiO_2 would be expected. Another example is the precipitation of phosphates on precipitating iron hydroxide floc.

Predicting Scale Formation

A variety of empirical and theoretical scaling index calculations have been used to predict the probability of mineral scale formation. Early methods of predicting the scale-forming tendency of water, range from simple equilibrium saturation indices, to empirical indices based on experimental or field data. The two key examples of these are the Langelier and Ryznar indices.

Langelier Saturation Index

This was the first index to come into wide usage (1920s). This index is based on the saturation pH (pH_S) of $CaCO_3$ in water. The definition of the pH_S is the pH at which a given water is saturated with calcium carbonate. The first step is to calculate the pH_S of the water. Then determine the Langelier saturation index (LSI) by the difference between the actual pH and the saturation pH for $CaCO_3$, as shown in Eq. (15.3):

$$\mathrm{LSI} = \mathrm{pH} - \mathrm{pH}_S \tag{15.3}$$

$$\mathrm{LSI} > 0 \Rightarrow \text{Scaling}$$

$$\mathrm{LSI} \leq 0 \Rightarrow \text{Non-scaling}$$

As Langelier noted, the index is an indication of driving force and not a quantitative indication of scale formation.

Ryznar Stability Index

The LSI gives equal weight to pH and the dissolved solids content. This index is more predictive of the saturation state than the amount or severity of potential deposits. Ryznar (1938) developed a correlation between actual reported problems in the field with water chemistry, defining a new, empirical index shown in Eq. (15.4):

$$\mathrm{RSI} = 2\mathrm{pH}_S - \mathrm{pH} \tag{15.4}$$

$$\mathrm{RSI} > 6.0 \Rightarrow \text{Corrosive}$$

$$\mathrm{RSI} < 6.0 \Rightarrow \text{Scaling}$$

Ryznar Stability Index (RSI) gives more weight to the dissolved solids content of water than to the saturation state, so RSI should be more predictive than LSI of the severity of problems.

These first indices were an attempt to define the effect of water chemistry on scaling and corrosion. Both LSI and RSI were originally developed to enable better control of calcium and alkalinity adjustments in municipal water systems. Both are based on calculations of the solubility of calcium carbonate within limited ranges of temperature and dissolved solids. Both LSI and RSI assume that water supersaturated in $CaCO_3$ will form scale. The RSI assumes that below saturation, water is corrosive to iron. While water that is supersaturated in $CaCO_3$ may be scale forming, water that is subsaturated with respect to $CaCO_3$ may not be corrosive. Many similar indices are available for minerals such as calcium sulfate, calcium phosphate, magnesium hydroxide, and silica. Examples include the Stiff/Davies Saturation Index, the Larson and Buswell Index, and the Larson/Skold Corrosivity Index.

All indices are either inherently or intentionally limited in scope to make them easy to use. None of these methods considers all the complex factors in natural water that affect mineral solubility. In cooling tower applications, the inherent limitations of these simplified indices can give erroneous predictions of the scaling or corrosive tendency of the water. These limitations include:

- The effects of temperature and ionic strength are either ignored or severely limited.
- The solubility of other scaling species (besides $CaCO_3$) is ignored.
- The effects of soluble complexes (ion pairing) are not calculated.
- For new systems, a predicted pH based on the concentrated makeup water must be used, which is often in error.
- Simplifying assumptions are made about the carbonate equilibrium.

Simple indices are at best, rules of thumb, and should seldom be applied to cooling tower systems, even though from a practical view, indices are very easy to calculate and interpret. Today, the availability of computers and software that can consider the complex equilibria that occur in cooling systems makes simple indices obsolete.

Capabilities of Computer Models

The limitations of simple indices are not due to a lack of understanding of the problem, but to efforts to simplify the equations for general use. However, with the computer, rigorous calculations can be done much more easily and quickly. The effect of a wide variety of conditions, such as temperature, pH, ionic strength, common ion effects, ion pairing, and various inhibitors, can be determined rapidly and easily using a computer model. With these methods, a profile of the scaling tendency of the makeup water for a cooling tower, can be readily determined. With empirical correlations, accurate predictions of the corrosion rate provided by various treatment programs can also be obtained.

Accurate temperature adjustments to equilibrium constants and compensation for ionic strength effects can be calculated. The models can include large databases of soluble and solid/solution equilibrium constants.

Also important are the calculation of the effect of soluble complexes, where ion pairing can increase the solubility of other less soluble minerals.

The real benefit of computer models comes from the predictive ability of this software. These models can predict the impact of changes in operating cooling systems as the water concentrates and equilibrates with the air. This can include calculation of the pH that will result in a system under various conditions, based on the effect of soluble gases and calculation of the CO_2 equilibrium in a system. For scaling systems, a calculation of the amount of potential deposits can be performed. Incorporation of oxidation/reduction equilibria allows the prediction of corrosion potentials as well. Empirical correlation of the effect of water chemistry on corrosion can enhance the oxidation/reduction equilibria calculations to provide better accuracy.

Some models have been adapted to water treatment use by addition of information on the performance of treatment chemicals. For example, the effect of deposit control chemicals on equilibrium behavior of potential mineral scale can be predicted. This is valuable with sparingly soluble inhibitors such as phosphate and zinc, where the solubility behavior of inhibitor components can be modeled. Finally, the capability to graphically compare the effect of operational parameter changes on water chemistry allows “what-if” scenarios to be evaluated safely, without experimentation on an operating system. The clear advantage of computer models over simple indices is obvious (Fig. 15.9).

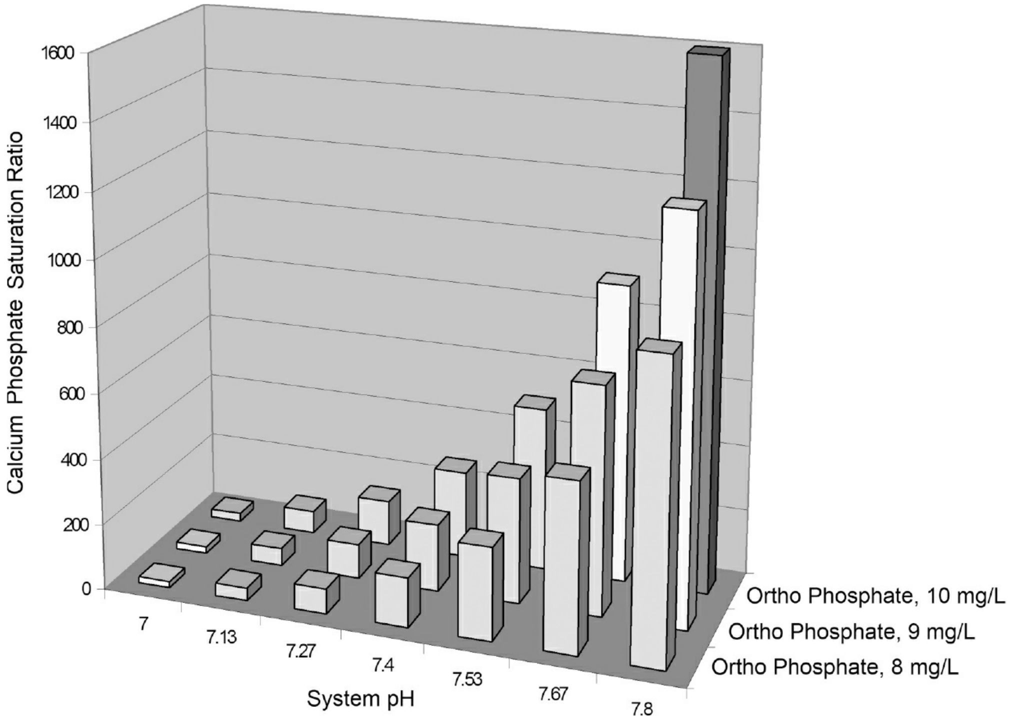


FIGURE 15.9 Sophisticated computer models can quickly evaluate solubility over a wide range of conditions and consider complicated ionic interactions in solution, including inhibitor effects. In this graph, higher saturation ratio indicates lower solubility of calcium phosphate.

Fouling Deposition

Fouling is the aggregation and settling of insoluble material suspended in water through physical processes. Fouling can be caused by a variety of sources:

- Suspended solids—Scrubbed into cooling towers through contact with air or from turbid makeup sources. Road dust, suspended silt, and clay deposits are commonly seen.
- Organic contamination—Contamination of tower water by process fluids that leak into the water results in organic fouling. Oil fouling in refinery systems is a common example.
- Iron and manganese—Soluble Fe^{+2} and Mn^{+2} ions may be found in well water. These ions are oxidized in the cooling system water. The insoluble oxidized form will behave like other particulate material.
- Corrosion products—These materials can either precipitate in place at

the corrosion site or be carried by the water and precipitate in other places in the system.

- Treatment products—Overdosing some treatment chemicals can cause precipitation, generally by a scale formation mechanism.
- Microbial growth—Slime formed by bacteria acts as a binder for other foulants such as silts and scales.

The process of deposition by suspended solids will be briefly described, since this is most widely encountered. Knowledge of the interaction of the particles in suspension is valuable to understand how dispersants can prevent fouling from suspended solids. Fouling by organic contamination such as oils or other process leaks is due to the insolubility of these nonionic compounds in the highly ionic water. Oxidized iron and manganese or corrosion products carried into the system can behave much like suspended particles. Fouling by treatment products is primarily a scale forming mechanism due to precipitation of the treatment with calcium or other positive ions in solution.

Suspended Particle Interactions

The tendency for particles to settle out of solution depends on particle size, surface charge, and the attractive forces between small particles in solution. Larger particles will settle more quickly by gravity. For example, a handful of sand added to a bucket of water will settle rapidly. However, there will be some small particles that settle slowly or will not settle at all. Particles under 1 μm are generally non-settling.

The random motion of particles in solution results in collisions of the particles. This process can be aided by the flow of water in a cooling system. The colliding particles may or may not stick together. This process, called agglomeration, is controlled by the magnitude of the attractive and repulsive forces on the surfaces of particles. The particle surface properties are often more important than the chemical composition of the particle.

Attractive and Repulsive Forces

The size of the particle, its density, and surface charge are key factors in determining whether agglomeration occurs. Electrostatic charges exist on the surface of suspended particles in water. The surface charge develops either by adsorption of charged ions from the solution or by dissociation of surface molecules into the solution. The charge on the particle surface must be compensated by an ion of opposite charge (a counter-ion) nearby in solution. Many of these counter-ions, especially at high surface charge density, are tightly held near the surface. The rest of the counter-ions form a more diffuse ionic atmosphere around the particle, as shown schematically in Fig. 15.10. This distribution of charge is generally referred to as the electrical double layer.

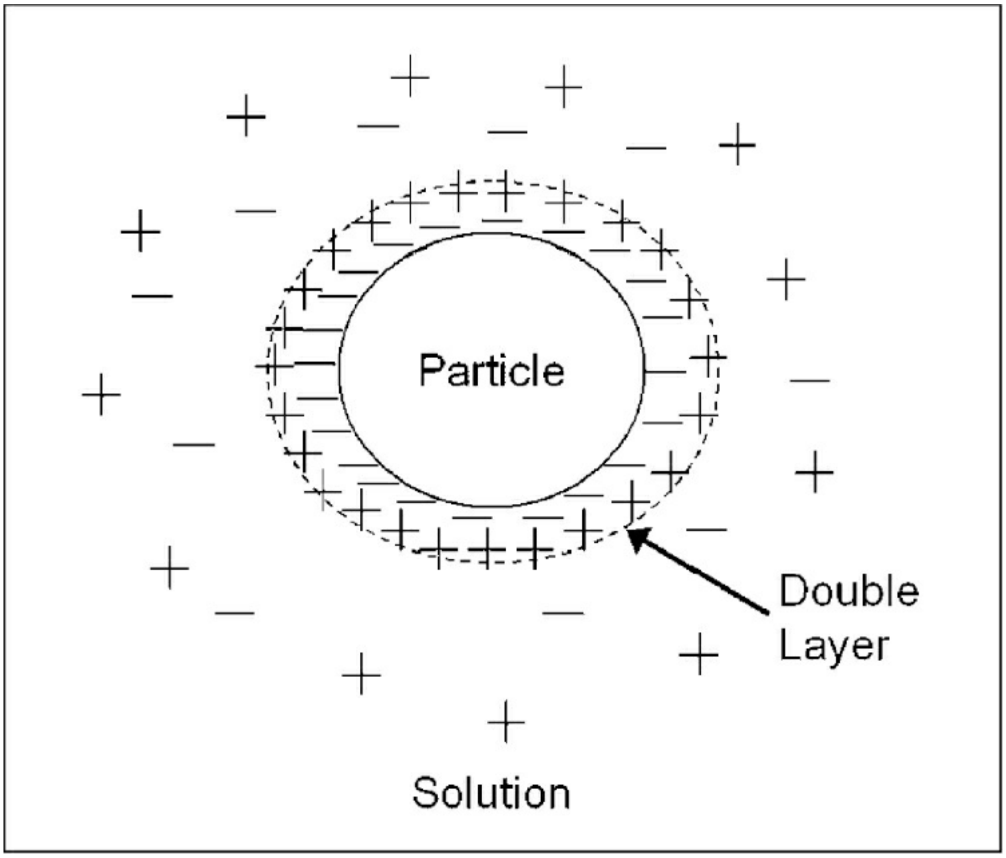


FIGURE 15.10 A suspended particle in water has a surface charge that is balanced by a layer of nearby ions in solution, which is called the ionic double layer.

The net effect is that each particle with its surrounding double layer is electrically neutral. When two particles approach each other, the ionic atmospheres of the two particles overlap. Energy is required to change the distribution of counter-ions so that this overlap can occur. In a stagnant solution, that energy is generally not available; hence, the particles repel each other, despite overall electroneutrality. In cooling water systems, the flow of water can provide the needed energy to remove the double layer, allowing the particles to come close enough to attract each other. In addition, the presence of divalent and trivalent cations can destabilize the particles and increase agglomeration. This is why materials like alum (containing Al^{+3} ions) and ferrous sulfate (source of Fe^{+2}) are used in clarification of water containing suspended material.

Agglomeration and Growth

As the agglomerated particles grow, larger particles begin to settle, just like a larger, single grain of sand. The more suspended solids in a system, the greater the possibility of fouling deposition. This allows for more collisions between particles, which can result in more agglomeration. Surface characteristics of the system have an effect upon the physical nature of the deposit once particles have settled. Thus, the potential deposition on a relatively rough surface such as mild steel, is greater than for a smooth surface such as copper or stainless steel. An increase in deposition potential also occurs when the depositing material consists in part of sticky particles such as microorganisms.

Suspended Solids Deposition Processes

Once fouling by suspended material begins, deposits may continue to grow indefinitely, or the rate of fouling may slow down. Kern and Seaton proposed a model where the rate of fouling would slow down asymptotically over time. This evolved from their observation that fouling in industrial heat exchangers often slowed to a low rate after sufficient time. Kern and Seaton proposed that the net fouling rate was the difference between a deposition process and a removal process, both of which occur simultaneously. The removal process can also be thought of as release of material back into the flow or re-entrainment. The possibility that both deposition and release exist simultaneously can be explained by turbulent flow phenomenon in water. As conditions fluctuate in a turbulent stream, deposition can occur in areas that are more quiescent. Removal can be due to bursts of turbulence at a surface that shear particles from that surface. Reduced deposition can also be due to increased turbulence, as deposits create a rough surface or as velocity increases through the reduced diameter of tubing. Turbulent flow in exchangers is well known to help minimize fouling.

Cooling Systems Deposits

Deposits in cooling systems can be composed of a number of materials. Following are the more common scales and foulants.

Calcium Carbonate

A common mineral scale in cooling water systems is calcium carbonate ($CaCO_3$). Its solubility decreases as temperature increases (inverse solubility). Solubility also decreases as pH increases. Calcium carbonate forms hard, tenacious scale and can exist as calcite, aragonite, and vaterite. Calcium carbonate formation depends upon the complex balance between calcium, carbon dioxide, bicarbonate, and carbonate in cooling water. Any change that drives the equilibrium reaction toward calcium carbonate (such as increasing the temperature or pH) will tend to cause precipitation. The same phenomena that describe lime softening reactions apply to the precipitation of this scale.

Calcite is the most stable form of calcium carbonate and can exist in a variety of crystal forms. Calcite is the form of calcium carbonate most often found in cooling systems (Fig. 15.11). Aragonite is less common and less stable than calcite. Calcite is the principal constituent of limestone, and aragonite is most commonly found in pearls. Aragonite generally forms at higher temperatures compared to calcite. Aragonite can have a variety of crystal structures, several of which include needle-like crystals (Fig. 15.12). Impurities in the water such as magnesium, strontium, or barium will sometimes cause preferential formation of aragonite over calcite, or increase the percentage of aragonite in mixed deposits.

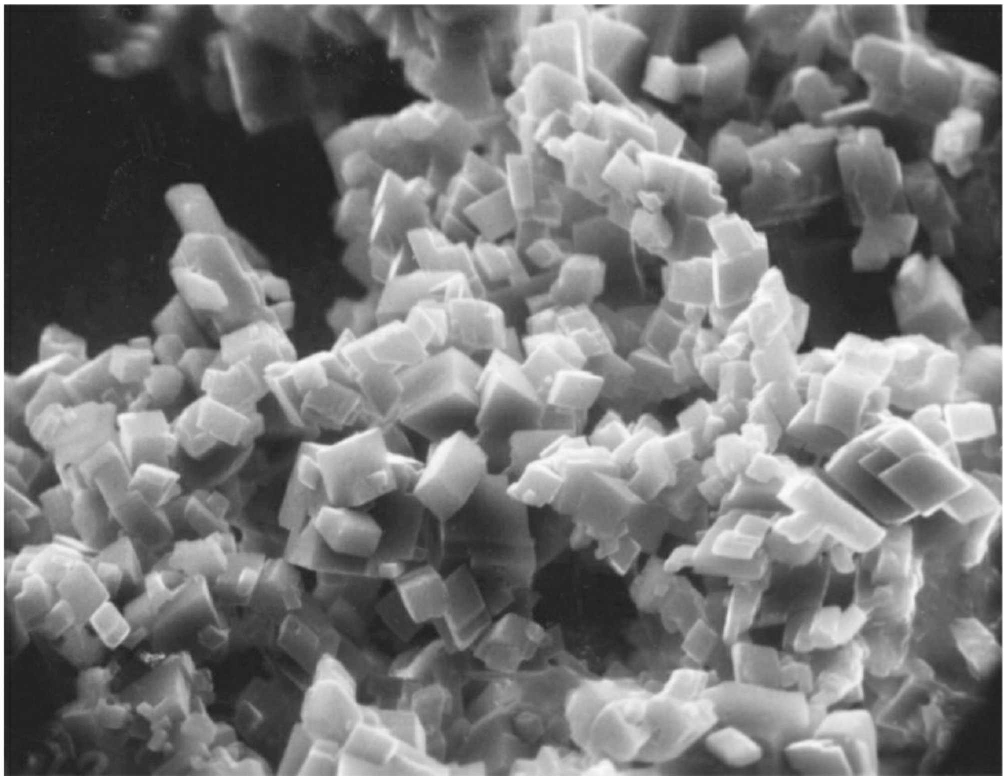


FIGURE 15.11 Example of calcite crystals, the more common crystalline form of calcium carbonate.

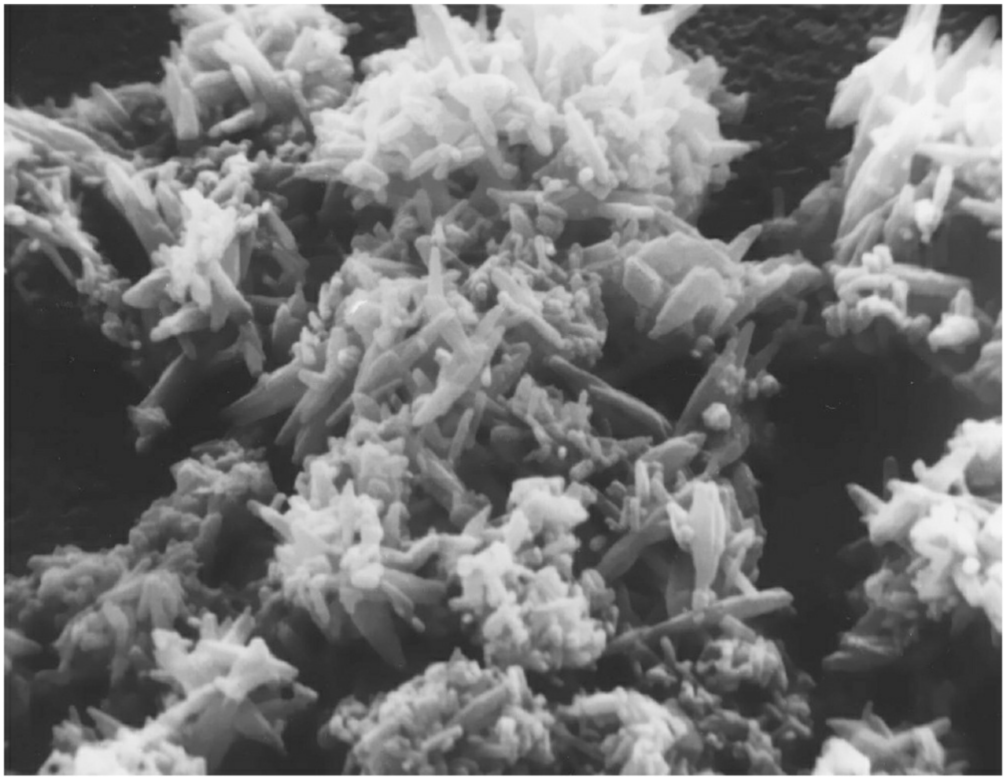


FIGURE 15.12 Aragonite is a form of calcium carbonate that sometimes appears as needle-shaped

crystals.

Under field conditions, calcium carbonate is white or light brown and might be combined with other minerals. If formed rapidly, calcium carbonate can be porous and amorphous in nature. Often, calcium carbonate deposits in cooling systems are a combination of calcite and aragonite.

Calcium Sulfate

Calcium sulfate is relatively soluble compared with other scales like $CaCO_3$, and is not often a problem in cooling water applications. This mineral is found in cooling towers operating at high concentration ratio such as in power generation and in brackish water applications. Sulfuric acid, used for pH control, will increase the sulfate concentration in cooling water. Potential forms of calcium sulfate are anhydrite ($CaSO_4$), hemihydrate ($CaSO_4 \cdot \frac{1}{2} H_2O$), and gypsum ($CaSO_4 \cdot 2H_2O$). Gypsum is the natural mineral form of calcium sulfate. Gypsum is directly soluble with temperature; the anhydrite form is inversely soluble with temperature. Gypsum is stable below 150°F (66°C), and anhydrite above this temperature. This means that gypsum could precipitate in cooler regions of the system like the tower fill, whereas the anhydrite might be found on a hot heat exchanger.

For precipitation to occur, calcium usually must be greater than 800 to 900 mg/L (as $CaCO_3$), and sulfate needs to be very high (>5000 mg/L as Na_2SO_4). This is illustrated in Fig. 15.7 shown earlier. Note in this figure that calcium sulfate is soluble at higher calcium values if the sulfate concentration is less than 5000 mg/L as Na_2SO_4. However, concentration mechanisms that occur under deposits or in small crevices can cause $CaSO_4$ precipitation, even though bulk water concentrations of calcium and sulfate ions may not be at these levels. Calcium sulfate deposits are generally mixtures of various forms, as is the case with $CaCO_3$. In many cases, gypsum is found with the anhydrite or hemihydrate forms.

Silica and Silicates

The terms silica and silicates are often used interchangeably, even though silica and silicate represent two distinct types of compounds. These terms should not be used interchangeably. Silica refers to SiO_2. Silicate refers to compounds, which are formed by reacting ionized silica (SiO_3^{-2}) with metals such as calcium, magnesium, aluminum, iron, zinc, etc. Clays such as kaolinite and illite are examples of silicates found in cooling water as water-borne silt deposits. The variety of forms indicates the complexity of silicon chemistry. Silica deposition is a result of polymerization of silicic acid or biological activity in the water. Silicate deposits are often due to coprecipitation with other minerals, precipitation with multivalent cations, and fouling by silt. Several of these processes may take place concurrently, making prediction of equilibrium solubility difficult.

When silica or silicate is found in either water or a deposit, the analysis results are reported as SiO_2, regardless of whether the compound present is silica or silicate. The use of SiO_2 in expressing elements identified in a deposit sample, whether silica or silicate is present, assumes that an oxygenated form of silicon (Si) is present. Proper interpretation of water and deposit analyses along with an understanding of the variables contributing to silica or silicate deposition, is critical for assessing and correcting operating conditions, which result in deposition.

Common rules of thumb have been used to indicate whether silica-based scale can occur. These rules may indicate a general tendency for scale to form but cannot consider the complexity of a cooling water system. Therefore, rules of thumb should be used with caution. Computer models for solubility prediction should be used, because simple indices or graphs cannot consider all the aspects of silica and silicate scaling accurately.

Silica Deposits

Silica scale (SiO_2) is extremely tenacious, highly insulating, and very difficult to remove. Silica deposits are usually found as amorphous silicon dioxide. Silica scale is unusual and may occur only when the level of SiO_2 in the recirculating water exceeds 150 mg/L and temperature is below 70°F (21°C). Silica forms an equilibrium in water between silicic acid (H_2SiO_3) and silicate ions (SiO_3^{-2}). The solubility of silica increases as the pH increases (more silicate ions), as shown in Fig. 15.13. However, pH usually cannot be increased enough to prevent silica deposition, because other minerals then become less soluble. For example, magnesium silicate ($MgSiO_3$) becomes a more serious scaling problem as the pH increases above 8.5; therefore, care must be taken not to trade SiO_2 scale for $MgSiO_3$ scale. The system should be monitored for scale very closely when running a high pH and high-silica concentration, because the formation of any scale will encourage the coprecipitation of silica and magnesium silicate.

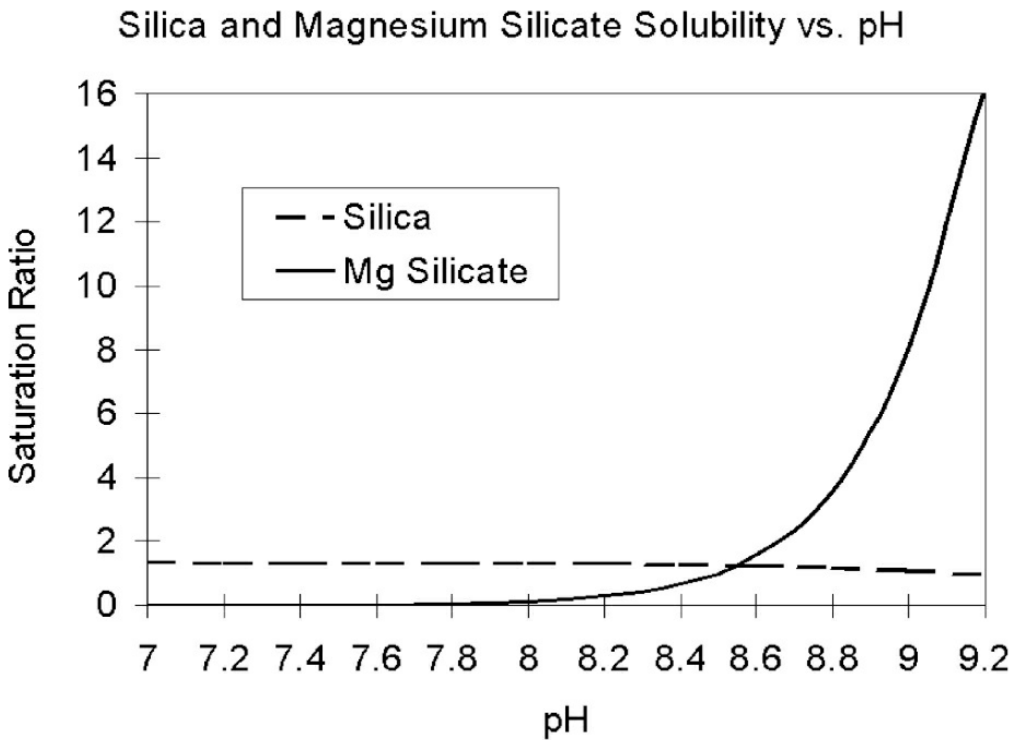


FIGURE 15.13 Silica solubility at 95°F (35°C) increases (lower saturation ratio) very slightly as pH increases, but magnesium silicate solubility decreases rapidly above pH 8.5.

Silica solubility increases with temperature. In high-silica waters, precipitation generally occurs in the cooler sections of a cooling water system. The maximum concentration of silica that can be tolerated in a recirculating cooling tower depends on several factors, such as inhibition of other minerals, corrosion control, biological control, and in general, the cleanliness of the system.

Living organisms such as diatoms can also be represented in deposit analyses as silica. These organisms remove silica from dilute solution to create their skeleton in precisely controlled structures of intricate design, almost perfect to molecular dimensions (Figs. 15.14 to 15.16).

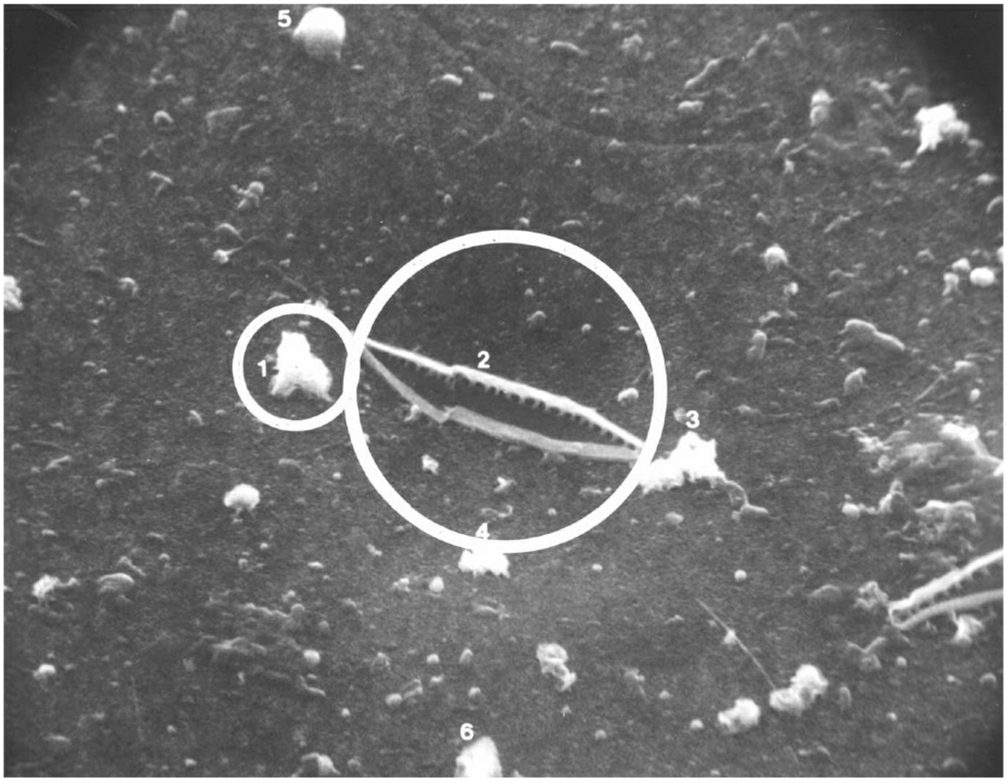


FIGURE 15.14 Scanning electron micrograph of particulates in a water sample.

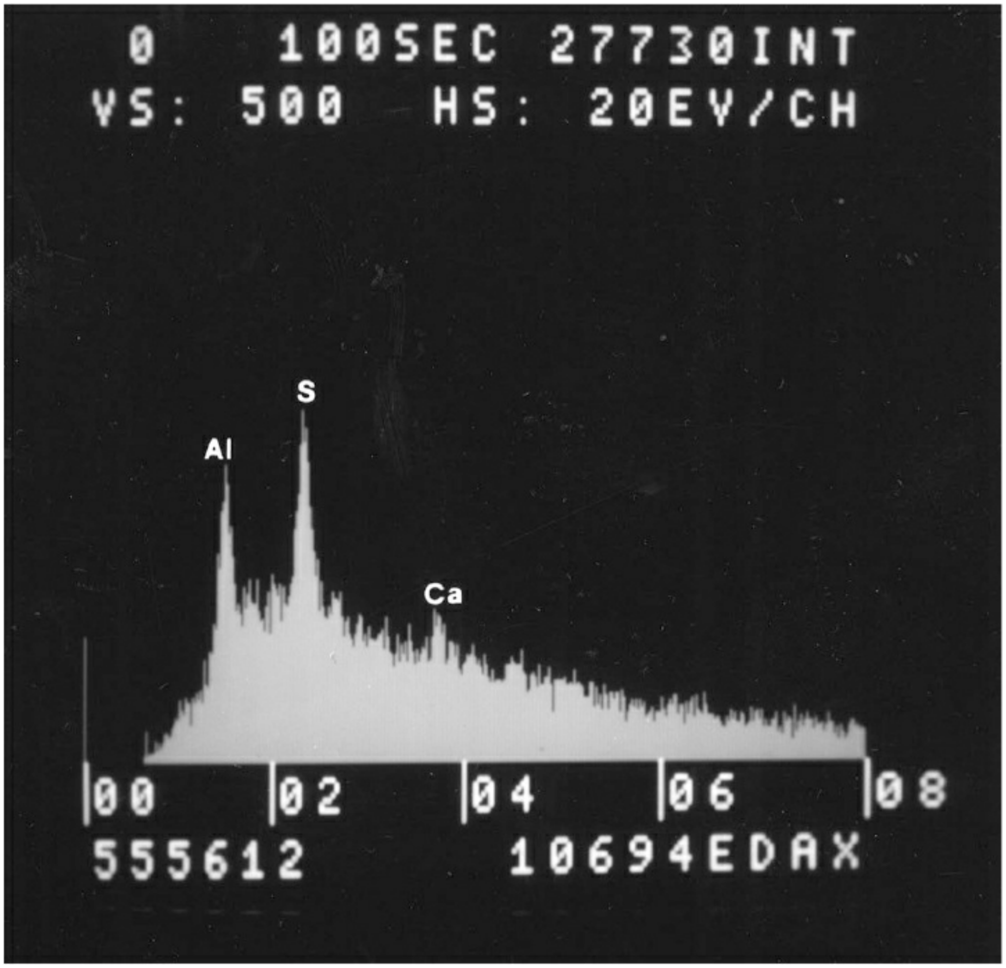


FIGURE 15.15 X-ray diffraction analysis of particles 1 and 3 identified as a precipitate containing calcium, sulfur, and aluminum.

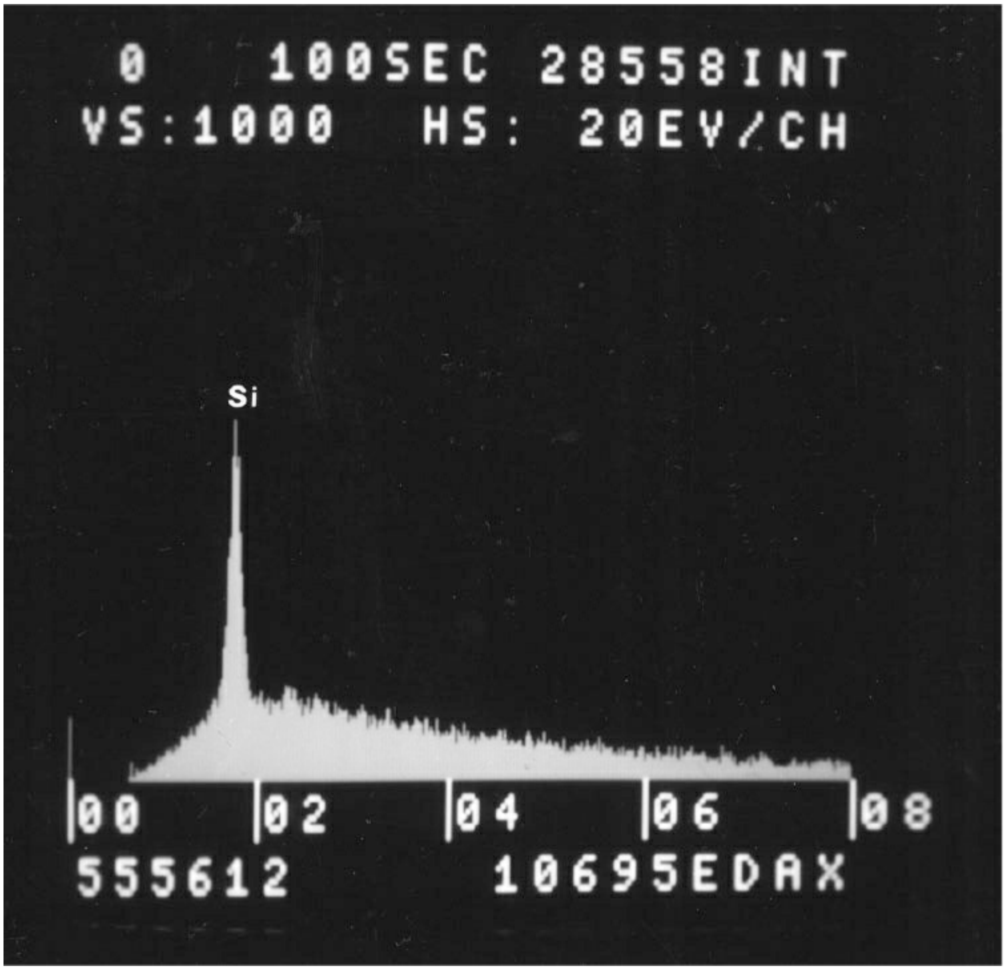


FIGURE 15.16 X-ray diffraction analysis of particle 2 identified as a diatom, which is mostly silica.

Magnesium and Aluminum Silicates

$MgSiO_3$ is a very tenacious, glassy-type scale that is difficult to remove except by mechanical or extreme chemical cleaning methods. Magnesium silicate precipitation is influenced greatly by pH, Mg, and SiO_2 levels. Generally, the pH must be greater than 8, depending on SiO_2 level, before $MgSiO_3$ precipitates. $MgSiO_3$ precipitation exhibits inverse solubility with increasing temperature. Consequently, scale will be more severe on heat transfer surfaces, especially when low-flow conditions exist.

Other factors that affect $MgSiO_3$ precipitation include high heat flux, bulk water temperature, and the Ca/Mg ratio. When the magnesium level is equal to or greater than the calcium level, the potential for $MgSiO_3$ scale greatly increases. $MgSiO_3$ precipitation normally accompanies precipitation of $CaCO_3$

in water containing appreciable silicate.

The presence of aluminum ions in water will reduce silica solubility. However, aluminum silicate deposits are most commonly due to deposition of silt.

Calcium Phosphate

Calcium phosphate, like calcium carbonate, exhibits an inverse solubility with increasing temperature and becomes less soluble as pH increases. The combination of calcium, orthophosphate, temperature, and high pH is extremely conducive to the deposition of calcium phosphate.

Calcium phosphate is much less soluble than calcium carbonate. As little as 1 to 2 mg/L orthophosphate (as PO_4) can result in extreme calcium phosphate scaling, when the calcium concentration is 200 to 1000 mg/L (as $CaCO_3$). Even in soft water localities, slightly higher orthophosphate concentrations can still create calcium phosphate scale. Figure 15.17 shows the solubility of calcium phosphate under a variety of cooling water conditions.

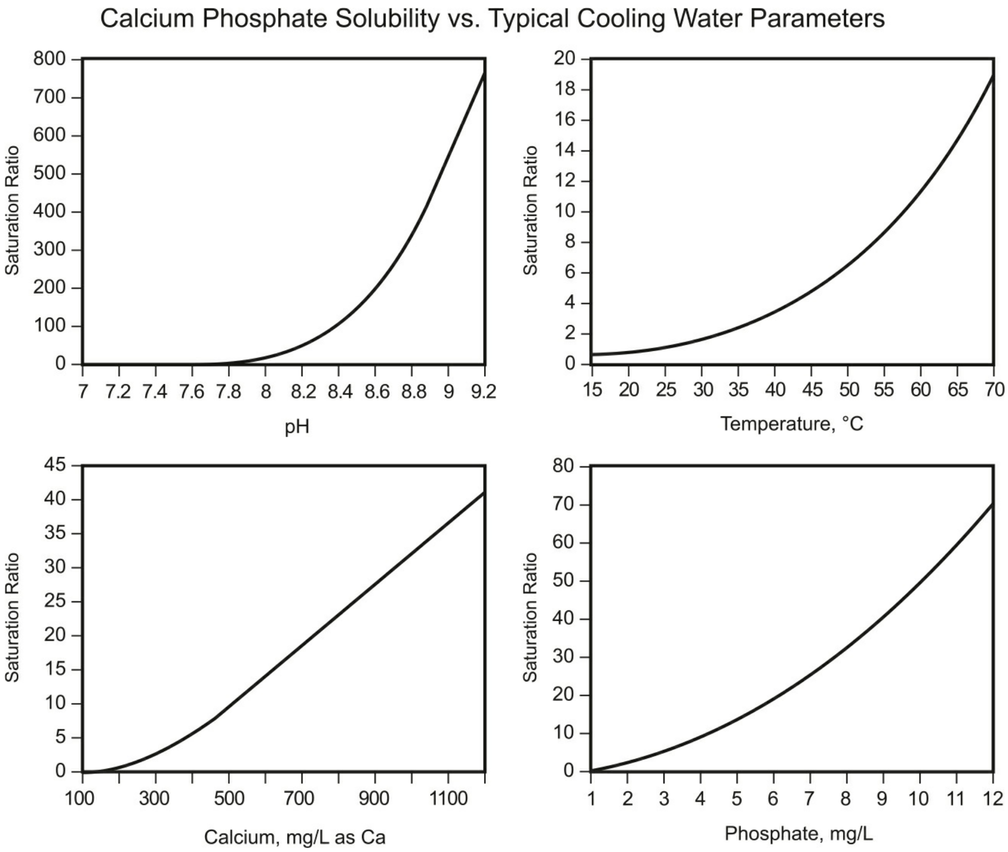


FIGURE 15.17 Calcium phosphate solubility as a function of pH, temperature, calcium concentration,

and phosphate concentration. Calcium is 625 mg/L as $CaCO_3$, orthophosphate is 2 mg/L as PO_4, and pH is 7.5 (except in graphs where calcium, phosphate, or pH vary). Other components are typical of cooling tower conditions.

Orthophosphate can come from a number of sources. In some regions of the world, the makeup water used for a cooling system can contain naturally occurring orthophosphate. In other places, the makeup water may contain phosphates that have been added as a corrosion inhibitor for the water distribution piping. These inhibitors could be either orthophosphate or polyphosphates, which are condensed phosphates that can break down to orthophosphate in water. This breakdown or reversion process is often aggravated by increasing temperature and pH that occurs in cooling systems. Polyphosphates are also used in some cooling system treatments, both as a corrosion inhibitor directly and as a source of orthophosphate through reversion. A third source of orthophosphate is the phosphonates that are often used for scale control. Several of these phosphonates are sensitive to degradation by oxidizing biocides used for microbial control. One of the degradation products is orthophosphate. Therefore, this is another example of the need for good control of cooling system operating parameters to minimize the potential for deposition from the various sources of orthophosphate.

A variety of calcium phosphate forms can exist, such as amorphous calcium phosphate, tricalcium phosphate, or hydroxyapatite (HAP). The initial stages of precipitation often produce amorphous calcium phosphate, which transforms over time into HAP. As a result, deposits containing calcium phosphate often contain mixed phases of calcium phosphate.

Aluminum ions can significantly affect the solubility of phosphate in cooling water. Aluminum phosphate is a highly insoluble white scale that forms whenever aluminum ions and phosphate are present in the water. This deposit is primarily a result of aluminum carryover from a clarifier. The aluminum ions can cause insoluble aluminum phosphate floc to form in the bulk solution, which then acts as a foulant. Soluble aluminum ions should be eliminated from the makeup water, when phosphate is present in the cooling water.

Zinc Deposits

Dissolved zinc ions are effective at corrosion inhibition, particularly for steel and cast iron. However, zinc ions can precipitate and contribute to scaling. Zinc-based scales are generally soft and loose. Zinc hydroxide, carbonate, and phosphate all occur, depending on the water chemistry and inhibitor programs in use. Each of these zinc precipitates is normally less soluble at higher pH (>7.5), and each precipitate has different solubility as a function of increasing temperature. Zinc hydroxide is less soluble at higher temperatures, zinc phosphate is more soluble at high temperature, and zinc carbonate is only slightly less soluble as temperature increases (Fig. 15.18). The solubility of zinc phosphate is one of the reasons why the combination of orthophosphate and zinc is a good corrosion control program at alkaline pH.

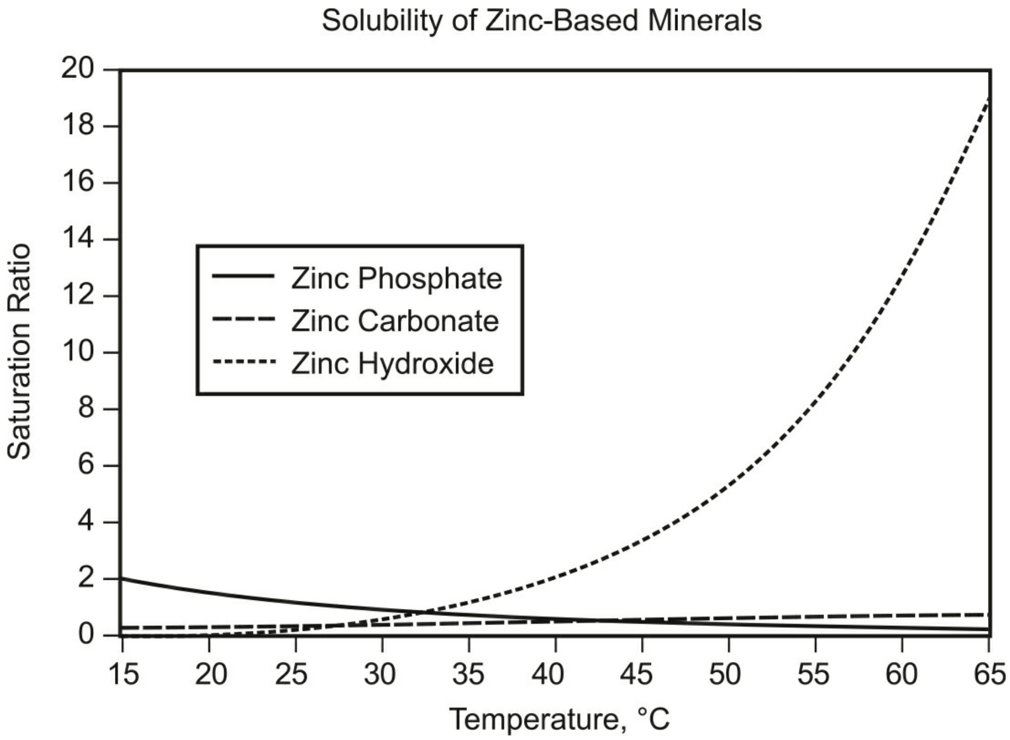


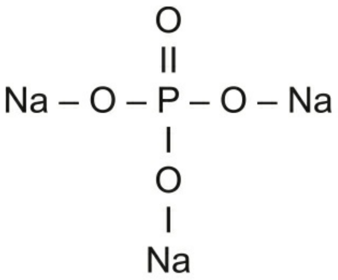
FIGURE 15.18 Solubility of zinc species as a function of temperature.

Zinc deposits can result from an overfeed of a zinc-based treatment program. Zinc carbonate ($ZnCO_3$) can also result from corrosion of galvanized metal. This "white rust" is usually found on the galvanized metal surface where the corrosion occurs, rather than in other parts of the system. White rust is covered in more detail in Chap. 16 on Cooling System Corrosion.

Zinc deposits are often non-tenacious but cause problems in low-flow heat transfer areas. However, zinc deposits can form on heat exchangers with higher flow, when overfeed conditions exist. When bulk precipitation occurs, the zinc-based scale that forms is not protective as a corrosion inhibiting film. As with all scale, this can lead to under-deposit corrosion. Use of specialized dispersants at higher pH (>7.8) will inhibit zinc deposition. The dispersants that are normally effective on calcium phosphate will generally prevent zinc hydroxide and zinc phosphate scale too.

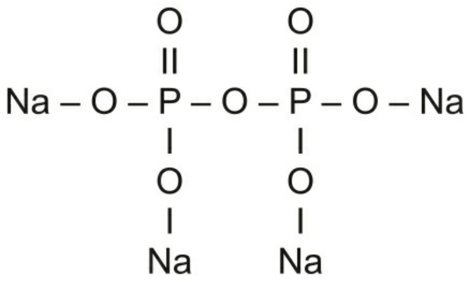
Calcium Polyphosphates

Polyphosphates have been used in water treatment for many years, but are used less frequently now because of reversion and environmental issues. Polyphosphates are commonly used in municipal water systems to prevent corrosion and minimize “red water” problems caused by soluble iron (ferrous ions) in the water. Polyphosphates are simply polymers of orthophosphate. A variety of forms exists from a simple combination of two phosphate molecules (pyrophosphate) to long-chain “glassy” phosphate molecules. Examples of phosphate molecules are shown in Fig. 15.19.



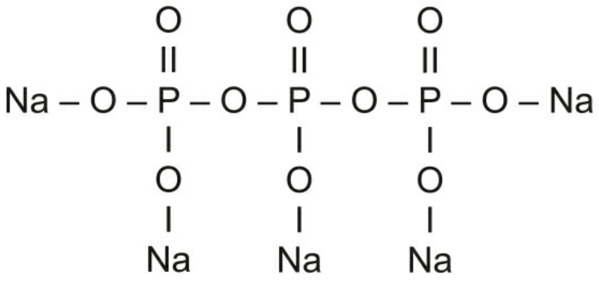
$$\mathrm{Na-O-\underset{\underset{\underset{\underset{Na}{|}}{O}}{|}}{\overset{\overset{O}{\|}}{P}}-O-Na}$$

Sodium Orthophosphate



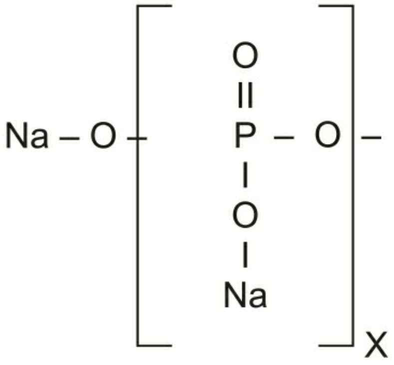
$$\mathrm{Na-O-\underset{\underset{\underset{\underset{Na}{|}}{O}}{|}}{\overset{\overset{O}{\|}}{P}}-O-\underset{\underset{\underset{\underset{Na}{|}}{O}}{|}}{\overset{\overset{O}{\|}}{P}}-O-Na}$$

Sodium Pyrophosphate



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

Sodium Tripolyphosphate



$$\mathrm{Na-O-\left[\underset{\underset{\underset{\underset{Na}{|}}{O}}{|}}{\overset{\overset{O}{\|}}{P}}-O\right]_X-Na}$$

Where X ⩾ 4

Long-Chain Glassy Phosphate

FIGURE 15.19 Various polyphosphate structures.

Polyphosphates create two problems in cooling water systems. First, calcium polyphosphates have limited solubility in typical cooling water conditions. Polyphosphates form a weak complex with calcium in water. The solubility will vary depending on the type and concentration of polyphosphate, calcium, temperature, pH, and other factors. Figure 15.20 shows the solubility of calcium pyrophosphate to illustrate some of the factors that affect its solubility.

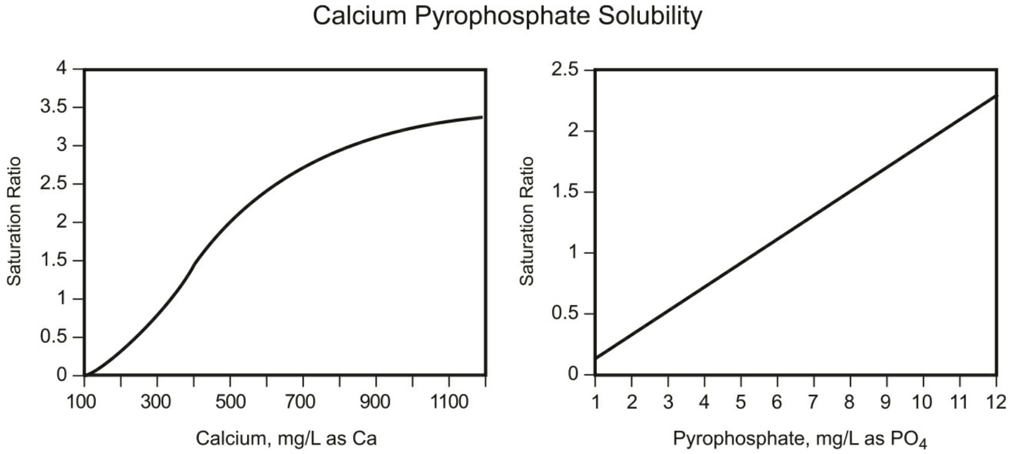


FIGURE 15.20 Calcium pyrophosphate solubility as a function of calcium and pyrophosphate concentrations. Pyrophosphate is 5 mg/L as PO_4 on the left, and calcium is 750 mg/L as $CaCO_3$ on the right. Temperature is 95°F (35°C), and pH is 7.5 in both charts.

Second, polyphosphate will break down to orthophosphate when dissolved in water. This is called reversion, and the resulting orthophosphate can cause deposition problems through precipitation of calcium orthophosphate. There are many factors that affect this reversion process, including the pH of the water, temperature, time, presence of trivalent ions, and microbial organisms in the water.

Calcium Phosphonates

Phosphonates are organic phosphate compounds, where the phosphorous is bonded directly to a carbon atom (C–P bond) on the organic molecule. There are various organic phosphate compounds available, which are effective scale control agents for calcium carbonate or calcium sulfate, for example. Phosphonates are much less prone to reversion to orthophosphate than are the polyphosphates. Examples include:

- AMP—aminotris-methylenephosphonic acid
- HEDP—1-hydroxyethylidene-1,1-diphosphonic acid
- PBTC—phosphonobutane-1,2,4-tricarboxylic acid
- PAPEMP—Polyamino polyether methylene phosphonate

Calcium salts of some phosphonates are insoluble and can contribute to scaling when misapplied. When applied at proper dosages, calcium phosphonate precipitation is minimal. The greatest problems occur if the phosphonates are overdosed or the calcium concentration is too high. As the calcium increases above 1200 mg/L, or the dosage of some phosphonates increases above 5 to 10 mg/L, precipitation can occur. Of the most common phosphonates, HEDP and AMP are the most sensitive to calcium precipitation. PBTC is the next most sensitive. PAPEMP is very soluble in the presence of calcium and is a very effective calcium carbonate inhibitor.

Iron

Iron oxides are often considered either a foulant or a scale. The cause of iron precipitation is different depending on the source of the iron, but the problem is equally serious. One of the most common forms of iron deposits is the oxide in corrosion products (rust). Iron is usually present to some degree in all cooling water deposits. Most often, an iron deposit looks like rust, but when combined with other minerals, iron deposits could appear as general foulants like silt.

Iron in Makeup Water

Subsurface waters (wells) may contain soluble iron in the ferrous form (Fe^{+2}). When water containing ferrous ions is aerated or chlorinated, the soluble ferrous ion is converted to the insoluble ferric form (Fe^{+3}). The result is a colloidal form of ferric hydroxide or ferric oxide [$Fe(OH)_3$ or Fe_2O_3], which exhibits a red color (red water). Iron oxides vary considerably in both physical and chemical characteristics: some are hard, dense, highly adherent deposits; others are loose, highly porous deposits. Some are reddish Fe_2O_3 deposits; others are black, highly magnetic iron oxide (Fe_3O_4) deposits. At normal pH values, iron oxide is not soluble in cooling water systems.

Corrosion Products

The corrosion of iron-based metals like mild steel or cast iron will release Fe^{+2}. If conditions are right, this can quickly oxidize to an insoluble, passive iron oxide film, which reduces corrosion. If the Fe^{+2} ions diffuse away from the metal surface before being oxidized, deposition will occur as fouling in other areas. Under non-passivating conditions, the initial Fe^{+2} can be oxidized to Fe_2O_3, and voluminous corrosion products can form at the site of corrosion. Figure 15.21 shows an example of iron corrosion products on a steel pipe.

FIGURE 15.21 Corrosion products containing iron oxides on a steel pipe can create voluminous deposits, almost plugging this utility service water pipe.

Influence of Bacteria

The precipitation of iron may be aggravated by the presence of iron-depositing bacteria. These bacteria are common in natural waters but less common in oxygenated cooling systems. The two most common species are *Gallionella* and *Sphaerotilus*. Both species oxidize soluble ferrous ions to insoluble ferric ions to create energy for growth. Under-deposit corrosion can often result from these deposits.

Iron Phosphates

Ferric phosphate ($FePO_4$) is seldom seen as a pure scale of just iron and phosphate, but often as a mixture with other minerals or suspended solids. This mineral is normally found in phosphate-treated systems, when iron is present at high levels in the makeup water. Typically, iron oxide or hydroxide will coprecipitate with calcium phosphate to form a yellowish-white precipitate.

Silt

The term silt refers to a combination of suspended, insoluble particles that can contaminate a cooling system. Silt commonly consists of silica and alumina compounds from the earth’s crust. River water silt particle size is 1 to 100 μm. Silt can generally enter a system in two ways:

1. Makeup water—Well waters are generally low in silt and suspended solids and of consistent quality. Surface waters (rivers or lakes) generally have higher amounts of silt, and the quality of water is greatly influenced by environmental factors such as runoff after a heavy rain or upsets in a lake. The quantity of silt in surface waters can vary considerably from day to day. Makeup waters with varying suspended solids are shown in Table 15.2.

Constituent (mg/L Except Conductivity)	Well	Well	Lake Hudson	Lake Superior	Willow River	Mississippi River
Aluminum (Al)	<0.1	<0.1	0.3	<0.1	0.2	0.4
Calcium ($CaCO_3$)	230	160	110	34	55	110
Magnesium ($CaCO_3$)	52	83	26	11	21	84
Silica (SiO_2)	9.7	9.6	5.9	2.5	10	9.0
Sodium (Na)	4.4	75	22	1.7	2.5	13
Chloride (Cl)	5.3	43	14	2.8	1.6	19
Sulfate (SO_4)	48	86	26	4.0	6.0	36
M alkalinity ($CaCO_3$)	240	220	120	45	62	150
P alkalinity ($CaCO_3$)	<10	<10	<10	<10	<1	<10
Conductivity (µS/cm)	560	790	320	100	150	410
Suspended solids (Total @ 105°C)	<1.6	<1.6	9.9	<1.5	9.3	25

TABLE 15.2 Differences in Makeup Waters from Wells, Rivers, and Lakes

2. Airborne contamination—The geographic location and local environment affect the type and amount of wind-blown dust entering a system. Cooling systems located in flat, open, windy areas accumulate silt faster than cooling systems in sheltered areas.

Mud and silt from turbid waters usually form hard, baked-on deposits on heat transfer surfaces. Mud and silt have a tendency to settle in low-flow (low-velocity) areas of a system, causing deposits. Additionally, mud and silt can be easily incorporated into other deposits, thus increasing the volume and insulating characteristics of the deposit. A deposit that is made up of mostly silica and aluminum is likely a silt deposit. The typical ratio of silica to aluminum is 3:1 as SiO_2 to Al_2O_3. There may also be small amounts of potassium or titanium in a silt-based deposit (Table 15.3).

Constituent	Form Reported	Percent in Dried Sample
Silica	SiO_2	52
Alumina	Al_2O_3	18
Iron*	Fe_2O_3	11
Calcium	$CaCO_3$	14
Potassium	K_2O	3
Titanium	TiO_2	2

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*Iron may be from corrosion products.

TABLE 15.3 Analysis of Deposit Caused by Silt

Manganese

The solubility properties of manganese are similar to iron. Like soluble iron, manganese is found in some groundwater sources. Unlike iron, some soluble manganese can be found in some river water sources. Manganese is not readily oxidized by dissolved oxygen, but will be oxidized by chlorine and hypochlorite causing a precipitate in cooling systems.

Several factors are peculiar to manganese fouling:

- The oxidation of manganese occurs at a moderate rate. As a result, some manganese may reach heat transfer surfaces in the soluble form, and then rapidly be oxidized, becoming adherent and very difficult to remove. On the other hand, some manganese oxidation occurs in the bulk water, forming a foulant, which then deposits on the heat transfer surface.
- The oxidation of manganese is autocatalytic in nature; that is, the oxidation reaction is catalyzed by the presence of manganese dioxide compounds. This means that deposits may be slow to appear, but eventual oxidation of a small portion of the available manganese can catalyze heavy deposition.
- Manganese dioxide is extremely tenacious and difficult to remove by

mechanical means normally used to clean heat exchangers and condensers.

- Manganese dioxide can cause under-deposit corrosion, particularly on copper alloys and stainless steel.

These factors make manganese a special problem unlike deposits caused by oxides of other metals. For example, deposits from corrosion of iron are objectionable, but generally not as tenacious or hard. Additionally, iron deposition is not autocatalytic, so the rate of iron oxide deposition does not escalate after the first deposits form.

[1] This phenomenon is discussed in greater depth in Mullins, J. W., *Crystallisation*, London: Butterworth and Company, Limited, 1972, pages 136-150.

CHAPTER 16

Cooling System Corrosion

Heat exchange equipment and piping in cooling water systems is made of various metals that are subject to the same problems that affect automobiles, tools, household plumbing, bridges and other metal products. If not properly treated, these metals seem to self-destruct when exposed to water in cooling water systems. This natural series of changes is called corrosion. Corrosion returns processed metals such as steel, copper, and zinc to their native oxide states as chemical compounds. This process of corrosion must be understood if long-term reliability of cooling water system operation is to be achieved.

Iron in its natural state is an oxide (e.g., Fe_3O_4, FeO, and Fe_2O_3). When processed into iron and steel, the oxygen is driven off to form pure iron (Fe°). Energy is required to transform the oxide into the metal. In the presence of water and oxygen, nature relentlessly attacks steel, returning the elemental iron (Fe°) back to an oxide, usually some combination of hematite (Fe_2O_3) and magnetite (Fe_3O_4).

In cooling water systems, corrosion is a serious problem. Cooling equipment designed for years of service may fail within months. If corrosion is not kept under control, heat exchangers will become inefficient because of corrosion deposit buildup, and equipment will be ruined because of leaks. All of these problems cost money in terms of increased maintenance, equipment repair or replacement, and lost production.

The annual global cost of corrosion is estimated to be $2.2 trillion according to The World Corrosion Organization.[1] Costs included the effect of corrosion of all types of equipment, not just cooling water systems. The costs included corrosion control methods, services, and the economic impact for specific industry segments, such as transportation, infrastructure, and industry.

The estimated costs were $6.9 billion/year for the electric utility industry and $17.6 billion/year for production and manufacturing. This study did not include indirect costs for lost production or lost reliability, so the true cost of corrosion is even higher.

Based on the information in this study, the global costs of cooling water corrosion, including lost efficiency and lost production, are in the billions of dollars per year. Fortunately, corrosion can be controlled with proper treatment and automated monitoring and control. This chapter will focus on what corrosion is, how corrosion occurs, and the problems corrosion causes.

Corrosion of Materials in Cooling Systems

Cooling water systems can be fabricated using a number of different metals and materials, each with unique corrosion issues. Some of the more common materials and corrosion mechanisms will be discussed here. For more detailed information, refer to *The Nalco Guide to Cooling Water Systems Failure Analysis*, 2nd ed.[2]

Carbon Steel

Mild or carbon steel is one of the most economical materials for construction of heat exchangers and cooling water systems. However, this metal is easily corroded in oxygenated cooling water. Carbon steel undergoes a wide variety of corrosion mechanisms, all impacted by the corrosivity of the water due to dissolved ions and dissolved oxygen. Carbon steel is sensitive to pH and suffers significant corrosion at low pH (acid conditions). The corrosion rate drops as the pH increases over 8.5, but corrosion increases at very high pH (caustic conditions over pH 12). As with other chemical reactions, corrosion increases with temperature. Consequently, high-heat-flux or high-temperature exchangers will suffer greater metal loss than transfer piping.

Corrosion products are generally brown or orange iron oxides. The corrosion products can form a protective oxide film on the metal surface that limits further corrosion, or the metal oxides can become a porous deposit that is not protective. Iron oxide deposits can also result from soluble iron in the water, which forms nonprotective deposits. Cooling systems that operate with carbon steel heat exchangers are particularly challenging. In these systems a very effective steel inhibitor along with good system control will pay dividends of improved operation and longer exchanger working life. A dense, passive film can form on the steel surface with the right inhibitor and concentration. Properly controlled cooling water programs can maintain corrosion at acceptable rates [generally considered <3 mpy (76 µm/y)]. Cooling systems that operate with carbon steel heat exchangers are particularly challenging and will benefit by using a very effective steel inhibitor along with good system control.

Copper Alloys

Copper and copper alloys are probably the next most commonly encountered metals in cooling water systems. These alloys are used when the metal is compatible with the process fluid to be cooled and the high thermal conductivity of copper is needed. Copper may be found in heating or cooling coils in building heating and chiller systems, domestic water systems, and in the molds of continuous caster systems in steel mills. In cooling tower systems, heat exchangers can often be made of admiralty brass, which contains copper, zinc, tin, and antimony or arsenic as alloying agents. In large power utility condensers, cupro-nickel alloys may be used to further minimize the damage from corrosion and erosion.

Copper alloys are more resistant to corrosion by oxygenated water than carbon steel. Copper alloys are on the borderline between immunity from corrosion and active corrosion. Oxidizing agents like halogens can push copper alloys into the corrosive state. The production of corrosion products is much less significant for copper alloys than for carbon steel, because copper alloys are more corrosion resistant. The cupric ions (Cu^{+2}) that form as an oxidation product of copper corrosion are much more soluble than the ferric ions (Fe^{+3}) from iron corrosion. Copper ions from makeup water or corrosion by-products can attach to less noble metal such as steel or aluminum surfaces setting up conditions for galvanic corrosion. Corrosion of copper and its alloys can be influenced by dissolved carbon dioxide, chloride, and ammonia. Chlorination of cooling water can increase corrosion of copper and its alloys. Precipitation of manganese dioxide can induce localized corrosion in copper alloys. Deposition of other materials on the surface can promote under-deposit corrosion. If the surfaces are kept clean, general corrosion rates of less than 0.2 mpy (5 µm/y) are considered acceptable. This is possible with effective treatment programs and system control.

Stainless Steel

Steel can be made “stainless” or highly corrosion resistant by inclusion of 11% or more chromium to form an alloy. There are many grades of stainless steel available. The most common are the austenitic stainless steels (304 and 316). The 304 grade contains 18 to 20% chromium and 8 to 10% nickel, hence 304 stainless steel is often called 18/8 stainless steel. The 316 grade adds 2 to 3% molybdenum in addition to chromium and nickel.

Stainless steel is very corrosion resistant in clean cooling water systems. In the presence of dissolved oxygen, a dense, highly adherent film of chromium oxide is formed on the surface, which prevents further corrosion. Stainless steel is an example of a self-passivating metal. Corrosion problems can occur in dirty systems, however. Stainless steel is susceptible to under-deposit corrosion, crevice corrosion, and stress corrosion cracking (SCC), particularly as the chloride content of the cooling water increases. SCC affects the austenitic stainless steels in waters that contain chloride. Other forms of stainless steel are more resistant to chloride stress corrosion cracking. However, the type 304 and 316 austenitic forms are the most commonly used. Surface cleanliness is important to minimize the tendency for under-deposit corrosion, crevice corrosion, and SCC.

Galvanized Steel

Galvanized steel generally involves a coating of zinc metal on the surface of carbon steel. This coating may be produced by dipping the steel in molten zinc or by electroplating. Galvanized metal is used in cooling water systems in panels or in piping. Galvanized metal is most commonly used in small to medium sized prefabricated cooling towers and evaporative condensers. The zinc layer is both a protective coating and a sacrificial anode. The zinc is much less noble than the underlying carbon steel. Therefore, the zinc will corrode sacrificially to protect the underlying steel. After the zinc corrodes through, and large surface areas are exposed, the steel will corrode at the same rate as ungalvanized carbon steel. At temperatures above 140°F (60°C), the polarity of the iron/zinc galvanic couple reverses, resulting in excessive corrosion of the iron. Galvanized steel should not be used above that temperature.

Some corrosion of galvanized coatings on steel is normal. When galvanized steel is exposed to a neutral pH, moderately hard water environment, a surface barrier of nonporous zinc carbonate and zinc hydroxide forms to prevent further rapid corrosion of the zinc coating. However, corrosion becomes excessive under certain conditions such as high pH or low hardness. Galvanized steel that has been attacked by excessive corrosion will have two different appearances. If corrosion is severe, all the galvanized coating will be removed, exposing the unprotected steel. In these cases, the steel can rust, giving the normal, rusty-brown or black appearance of corroding steel. In less severe cases, the zinc coating can be corroded to form what is known as "white rust" (Fig. 16.1). White rust is an unprotective form of zinc hydroxide or zinc carbonate on the surface of the metal. White rust corrosion is often identified because the deposit has a porous, soft, gelatinous, or waxy appearance. White rust can be very similar to a protective zinc oxide coating that forms on dull gray passivated galvanized metal. Both the protective oxide film and white rust are forms of zinc carbonate and zinc hydroxide. The key difference between white rust and the protective oxide film is that white rust is generally a more voluminous and porous deposit.

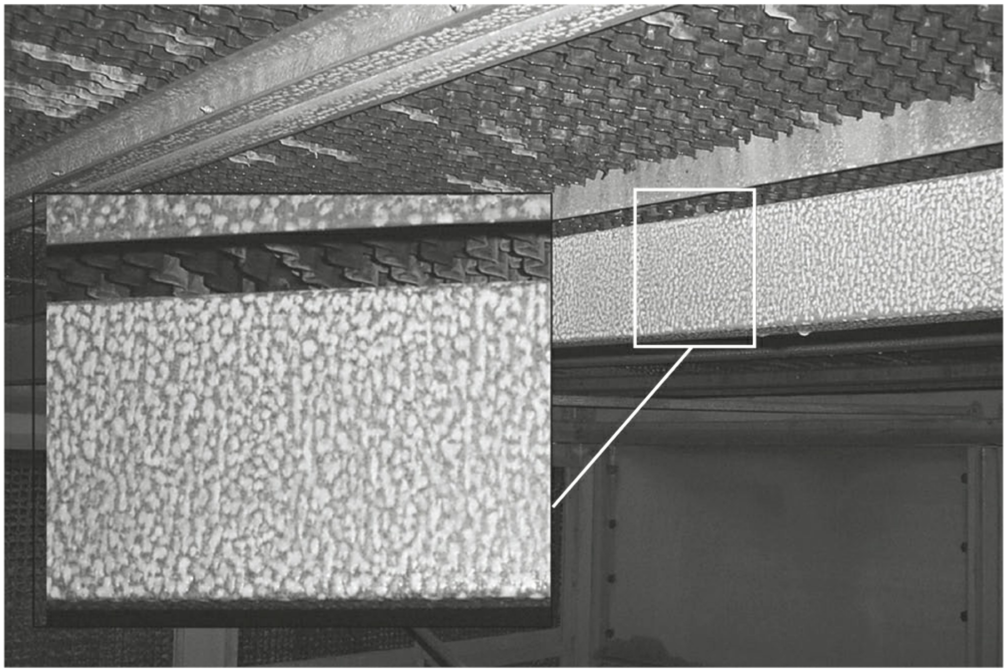


FIGURE 16.1 Example of white rust on a galvanized steel support beam under the fill section of a cooling tower.

White rust may appear suddenly and progress rapidly over the wetted galvanized areas of cooling towers. A surface covered by white rust is not resistant to further reaction with the aqueous environment, and rapid corrosion may continue. The term “wetted” refers to areas of cooling tower structures that are continually or occasionally wetted. The presence of white rust suggests operation out of the desired control window of pH and alkalinity, or improper passivation of a new or newly cleaned system. White rust corrosion can seriously damage the galvanized zinc coating and shorten the life of the cooling tower. Once the zinc layer has been consumed, corrosion of the mild steel may progress rapidly.

Evaporative condensers often use galvanized coils and tower components to reduce corrosion of the units themselves. Therefore, evaporative condensers often experience white rust.

Nonmetallic Materials

Various nonmetallic materials are used in cooling water systems, ranging from plastic or wood tower fill to concrete in the cooling tower basin. Depending on the environment, degradation of nonmetallic materials can be severe. While not strictly electrochemical corrosion reactions, chemical or biological degradation of nonmetallic materials can be a problem. In some cases, degradation may be worsened by improper treatment or poor control of the cooling tower operating parameters.

Wood in tower fill or support beams can be attacked both chemically and by microbial organisms. (Biological degradation is covered in Chap. 17 on Cooling Water Biology.) Chemical attack can result in delignification. Lignin is the binding material between the cellulose fibers in wood, and loss of lignin weakens the resulting wood structure. Studies have shown that delignification is caused, more by excessively high chlorine levels, than the pH of the water. Proper control of chlorination in alkaline pH treatment programs can significantly minimize the possibility of delignification.

Degradation of concrete can occur at high sulfate concentrations. Most cooling tower basins are now made with sulfate resistant concrete. Acidic pH excursions or poor acid mixing may damage concrete in basins or concrete that may be used to line piping. When feeding acid for pH control, it’s a good practice to use an acid-resistant dilution trough to prevent localized acid attack at the acid feed point.

Plastic components and rubber gaskets can be degraded by oxidizing biocides. Most composite materials now used are resistant to chlorine, but with high oxidant concentrations, problems can occur. Materials at and immediately downstream of the oxidizer injection point are most subject to oxidizer attack so attention to the oxidizer feed point and mixing are important to prevent localized feed point oxidizer attack. Common gasket materials may be rendered hard and inflexible, causing the seal to be lost. Plastic tower fill can be degraded by ultraviolet (UV) light, but degradation is minimized by both UV absorbing additives (sunscreen for the plastic) and the location of fill inside the towers.

Therefore, while degradation of nonmetallic components is not often considered a corrosion problem, good system control is necessary to maintain all parts of the system in the best condition.

The Corrosion Process in Cooling Systems

National Association of Corrosion Engineers (NACE), considered to be one of the world's leading authorities on industrial corrosion, defines corrosion as "the deterioration of a material, usually a metal, that results from a reaction with its environment". Corrosion can take many forms; some are oxidation/reduction reactions, while others are physical reactions to the environment or operating conditions. An understanding of corrosion mechanisms helps to identify appropriate corrosion control techniques.

The Local Cell Model

Corrosion is a complex process that can be understood with a simple electrochemical cell, shown for iron in Fig. 16.2. The corrosion cell process can be divided into four steps:

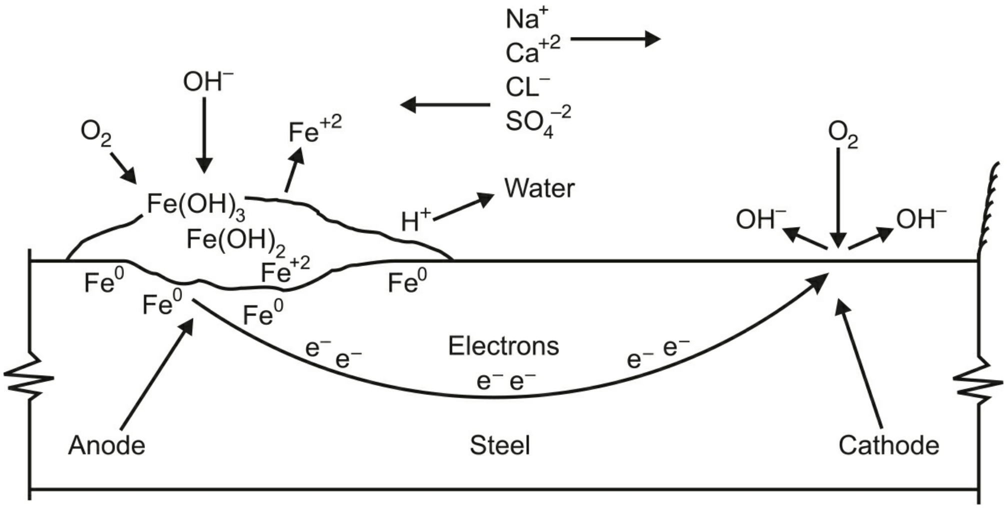


FIGURE 16.2 Metal dissolves at the anode and oxygen is reduced at the cathode in a typical corrosion cell on steel.

1. Metal loss occurs because of metal oxidation at the anodic area (anode).
2. The formation of metal ions from the metal releases two electrons that flow through the metal.
3. The electrons react with an oxidant at the cathodic area (cathode).
4. Ions or molecules in solution diffuse to each part of the corrosion cell.

The electron must be thought of as one of the reactants in this process. The anode gains a more positive potential by losing electrons. The cathode moves to a more negative potential because the cathodic area is gaining electrons. The potential difference created in the metal by differences at anodic and cathodic areas is the driving force for the corrosion process. The potential is like the pressure in a water line; the higher the pressure, the higher the flow can be when the line is open. The rate of corrosion is proportional to the current flow (flow of electrons) that results from the potential difference between the anode and cathode. Higher potential can support a higher flow, and thus, a higher corrosion rate.

Diffusion of ions and oxygen through the water occurs for two reasons. Ions diffuse to the surfaces to balance the charges that build up on the metal, because the electroneutrality of the system must be maintained. Cations diffuse toward the cathode to balance the excess of electrons that create a negative charge in these areas. Oxygen diffuses toward the cathode to accept electrons from the metal. The oxygen is reduced by the electrons and forms hydroxide ions, under cooling water conditions. Anions diffuse toward the anode to balance the positive charge created by the metal ions (like Fe^{+2} for iron) that are released into solution by the corrosion process.

While the local cell model is a convenient picture of the process, the anodes and cathodes typically do not stay in one place on the metal surface. Every metal surface is covered with innumerable microscopic-sized anodic and cathodic areas. These sites usually develop from surface irregularities from forming, extruding, and other metalworking operations. Differences in composition of the surface caused by different microstructures in the metal can create an electrical potential difference on the metal surface. Dissolution of metal and reduction of oxygen can occur at any site on the metal surface. An exception to this is that the anode will be stationary during pitting corrosion, or corrosion at a metallurgical feature, such as a crevice or defective weld.

The local cell model is useful to give a mechanistic framework for corrosion processes. This model illustrates the four component processes of corrosion. If one part of the process is stopped, the entire process can stop. Therefore, corrosion control can be based on stopping any of the four components: the anodic reaction, the cathodic reaction, the flow of electrons through surface films, or diffusion of ions to the metal surface.

Anodic Reactions

The reactions at each site of the electrochemical cell are called half-cell reactions, because together, the two reactions form a complete cell. The anodic reaction is the oxidation of the metal to metal ions. The anodic half-cell reactions for iron-based metals and for copper are shown in Eqs. (16.1) and (16.2):

$$\mathrm{Fe^0 \rightarrow Fe^{+2} + 2e^-} \tag{16.1}$$

$$\mathrm{Cu^0 \rightarrow Cu^{+1} + e^-} \tag{16.2}$$

The relative tendency for the anodic reaction to occur is referred to as nobility. Noble metals (gold and platinum) have a lower tendency toward corrosion and require higher potentials for corrosion to occur.

Cathodic Reactions

Cathodic reactions involve the removal of electrons from the metal by the reduction of oxidizing agents. Dissolved oxygen (O_2) in the water moves to the cathodic area and completes the electric circuit by accepting the electrons that are flowing to the cathode. As a result, hydroxide ions (OH^-) are formed at the surface of the metal. Equation (16.3) shows the common cathodic reaction in cooling systems:

$$\mathrm{\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^-} \tag{16.3}$$

At low pH (<5), the hydrogen ion (H^+) can take the place of oxygen and complete the electrical circuit, as shown in Eq. (16.4).

$$2H^+ + 2e^- \rightarrow H_2 \tag{16.4}$$

The lower the pH, the faster corrosion can take place, because there is more H^+ in solution to accept electrons at the cathodic sites. (Remember, pH is a logarithmic scale.) Because most cooling systems operate in the pH range of 6.5 to 9.5, the reduction of H^+ does not occur. The primary cathodic reaction is the reduction of oxygen [Eq. (16.3)].

Secondary Reactions

These are the reactions that the primary corrosion products undergo in order to form stable corrosion products. The secondary reactions are critical in determining whether the oxide layers that make up the corrosion product deposits will retard or accelerate the corrosion process. Inhibitors can participate in these secondary reactions to form protective layers.

Ferrous Metals

Rapid conversion of ferrous ions (Fe^{+2}) to ferric ions (Fe^{+3}) is essential to the formation of stable, protective layers of ferric oxide on steel. The most stable form is FeOOH, commonly known as gamma iron oxide. The oxidation of the ferrous ions must occur very near the metal surface to form a protective film. If ferrous ions diffuse farther away from the surface before becoming oxidized, the resulting iron oxide, can form a loose, nonprotective deposit.

Corrosion inhibitors can have three common actions on an iron surface:

1. The inhibitor can directly oxidize the ferrous ions near the metal surface, to the stable gamma iron oxide film. Chromate and nitrite act as oxidizers to form gamma iron oxide, which prevents corrosion of steel.
2. The inhibitor can catalyze the reaction of oxygen with ferrous ions near the metal surface to form the gamma iron oxide film. Orthophosphate and alkalinity are examples of catalysts in the corrosion inhibition process.

3. The inhibitor can absorb onto the oxide surface and strengthen the film against chloride penetration. Molybdate works in this manner.

Copper Alloys

Two oxides of copper may be formed by corrosion reactions. The formation of cupric oxide layers is detrimental and will not prevent corrosion, while cuprous oxides are more protective. Cuprous oxides are less soluble and more stable than cupric oxides. Even though the cuprous oxide can reduce corrosion of copper, this oxide film is not as protective on copper as the oxides of iron are on steel. For copper, corrosion inhibitors that form a film on the surface provide the best inhibition of the dissolution of copper at the anode and transfer of electrons at the cathode. (See Chap. 19 on Cooling Water Treatment and Control.)

Galvanic or Electrochemical Series

Galvanic corrosion is a special form of the general corrosion reaction. This form of corrosion results when two dissimilar metals are connected and exposed to a water environment. One metal becomes cathodic and the other anodic, setting up a galvanic couple or galvanic cell. For example, when copper and steel are connected in water, steel becomes the anode, and copper is the cathode. The metal loss occurs at the anode, so the steel corrodes at a faster rate, and the copper is protected from corrosion. Galvanic corrosion can be relatively common in cooling systems, for example, this occurs when a brass sample valve is placed on a steel pipe without separation by an insulating coupling.

Corrosion rate in a galvanic couple is dependent upon two factors:

1. What metals are connected
2. Relative anodic to cathodic surface areas

A galvanic couple in solution creates an electrical potential difference between the two metals. The electromotive or galvanic series illustrates the magnitude of that difference (Fig. 16.3). A pair of metals that are far apart in this table will have a greater potential difference (hence faster corrosion rate) than two metals that are close to each other in the table. The metals near the cathodic end of the chart are considered passive or noble metals. The metals near the anode end of the chart are considered active metals.

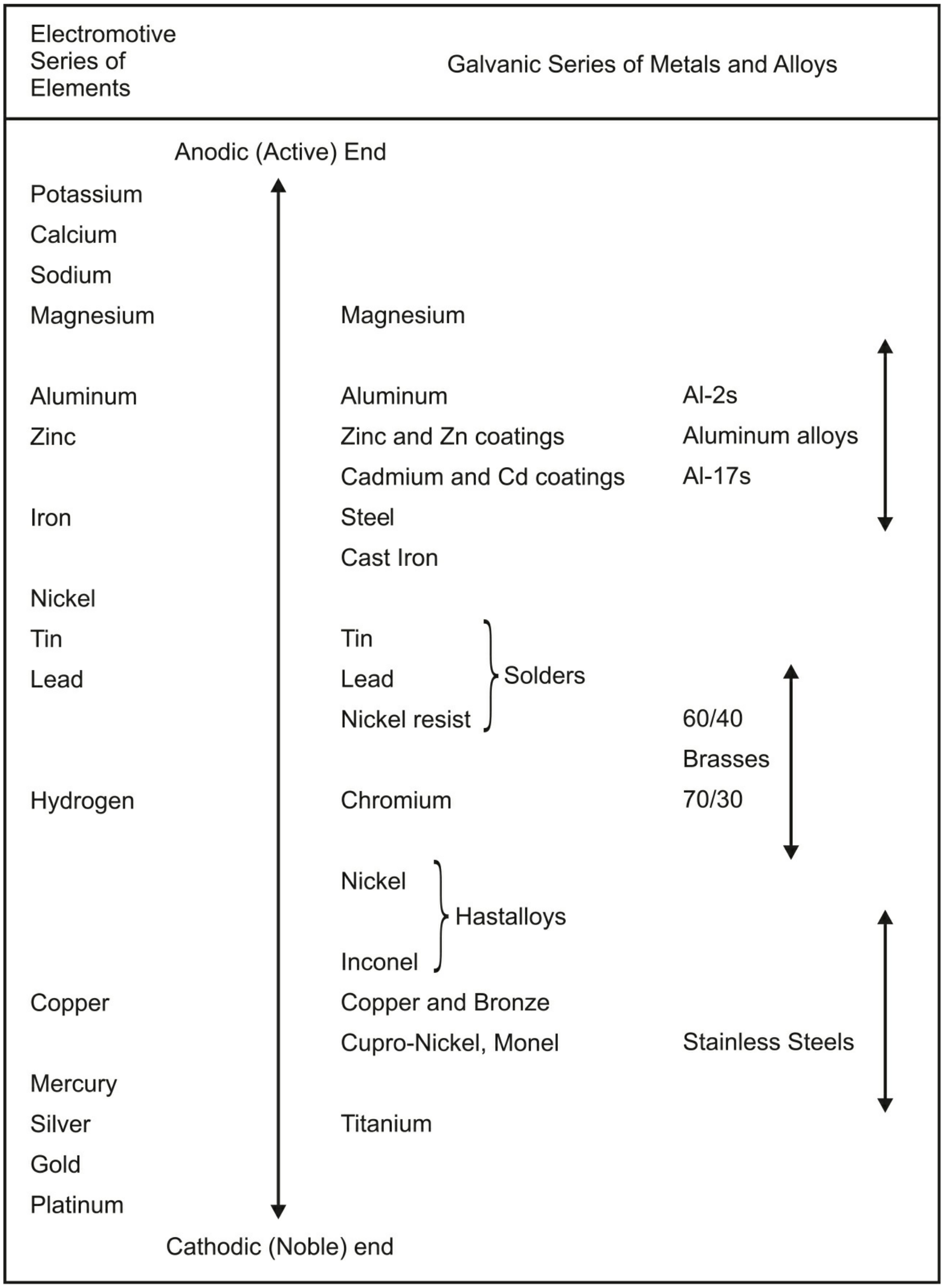


FIGURE 16.3 The electromotive series shows the relative potential of any two elements or metals in a galvanic couple.

The relative size of the anodic and cathodic areas determines the rate and type of corrosion. A larger cathode coupled to a small anode will cause higher corrosion and often pitting-type corrosion. A smaller cathode joined to a large anode will result in a lower corrosion rate and more general corrosion loss

(Fig. 16.4). These area relationships hold true as long as other factors influencing the system (e.g., temperature, conductivity, oxygen concentration, velocity, etc.) are equal.

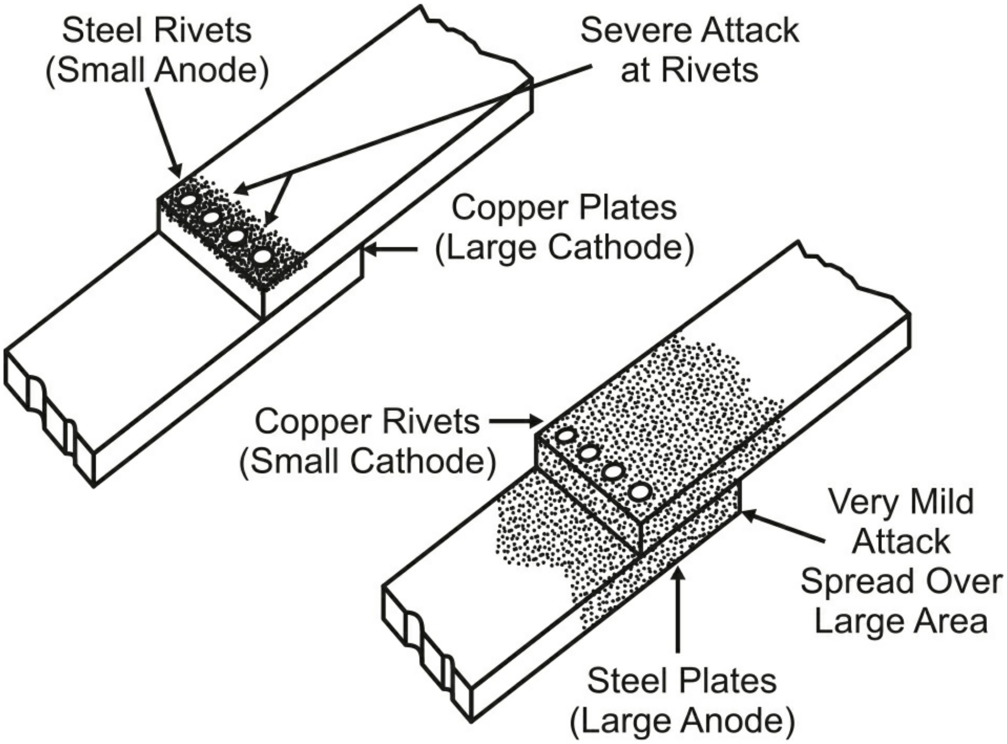


FIGURE 16.4 The rate of galvanic corrosion depends on the ratio of the anode area to the cathode area.

Another type of galvanic corrosion that occurs in cooling water systems are when ions of a more noble metal, such as copper in solution are "electrodeposited" on the surface of a less noble metal, such as steel or aluminum. This happens when the copper ions participate in the cathodic corrosion reaction and are reduced to copper metal on the surface. The copper ions take the place of oxygen in the cathodic reaction, as shown in Eq. (16.5):

$$Cu^{+} + e^{-} \rightarrow Cu^{0} \tag{16.5}$$

If enough copper metal is plated onto a more active metal surface, localized galvanic corrosion can occur. Aluminum is particularly vulnerable to galvanic corrosion from copper in cooling water. Figure 16.5 shows an example of this type of galvanic couple from copper plated onto a mild steel corrosion coupon.

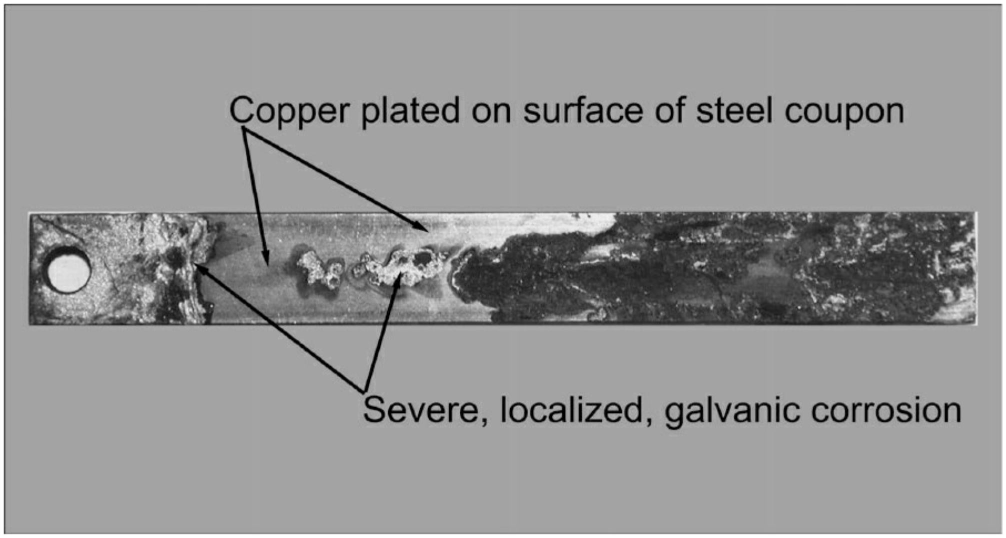


FIGURE 16.5 Example of galvanic corrosion due to the direct coupling of dissimilar metals. In this case, the galvanic couple is formed between the mild steel coupon and the electrodeposited copper on the steel coupon.

The Role of Oxygen in Corrosion

The oxygen concentration will affect the corrosion rate, either by increasing corrosion or by passivating the surface, which prevents corrosion. A low oxygen concentration causes a low corrosion rate, because the diffusion of oxygen to cathodic sites is limited. As the concentration of oxygen increases, diffusion increases, and corrosion rate increases. As oxygen concentration increases further, the corrosion rate may reduce again because the high oxygen concentration rapidly oxidizes ferrous ions near the metal surface to form a protective film. High oxygen concentration can accelerate the formation of dense, adherent passive films on the metal that diminish or even prevent further corrosion. Figure 16.6 shows the effect of oxygen on the corrosion rate in cooling water conditions.

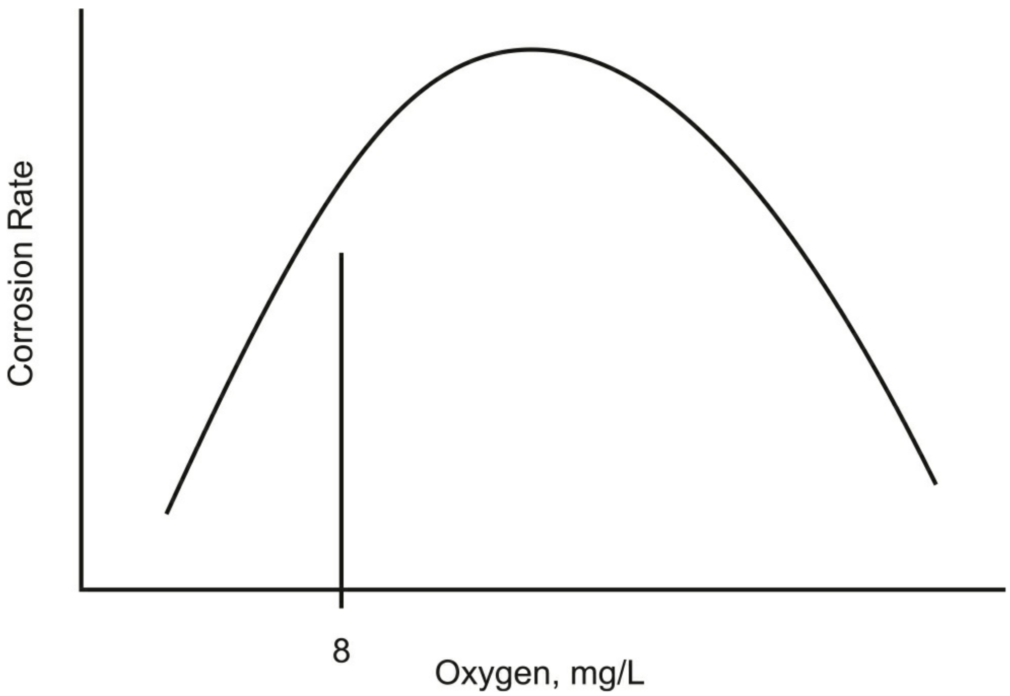


FIGURE 16.6 Effect of oxygen concentration on mild steel corrosion rate under cooling tower system conditions.

The oxygen concentration of the water varies, depending on the type and characteristics of a cooling system. The constant aeration as the water passes over a cooling tower will maintain oxygen saturation. This provides enough oxygen to support corrosion in open recirculating cooling systems. In closed systems, generalization about the oxygen concentration is more difficult. The oxygen concentration will be depleted over time in a truly closed system (no leaks). The loss of oxygen happens faster at higher temperature in closed water systems. Closed systems with leaks or systems that have open storage tanks will never lose all the dissolved oxygen, unless the water temperature is over 180°F (82°C), where oxygen solubility is very low.

Polarization and Corrosion Rates

The rate of either corrosion reaction (at the anode or at the cathode) is reduced by polarization of the metal surface, which occurs in several ways. First, a passive film of metal oxides or corrosion inhibitor can slow down the anodic corrosion reaction (metal loss). In the case of iron, a passive iron oxide film will reduce the dissolution of Fe° at the anode. Second, if the oxygen concentration in the solution is low, the lack of oxygen at the cathode will reduce corrosion. A final example is that cathodic reaction products like hydroxide (OH^-) can remain at the metal surface, forming a layer that prevents further reduction of oxygen by electrons in the metal. Figure 16.7 shows how a layer of hydroxide ions can form on the cathodic surface from the reaction of oxygen and water with electrons from the metal. The net effect of the hydroxide ion layer is a reduction of corrosion rate.

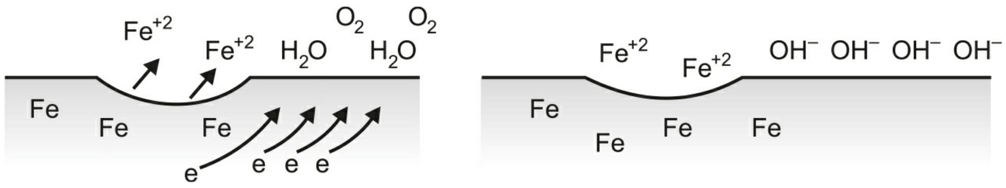


FIGURE 16.7 Polarization of the cathode by a concentrated film of hydroxide ions.

Removing or disrupting these anodic or cathodic barriers causes depolarization, and will restart the corrosion process. Several factors can lead to depolarization. One example is lowering the pH of the water, which increases the concentration of the hydrogen ions. These ions can then react with the hydroxyl ion formed at the cathode, removing the OH^- film and depolarizing the cathode. A lower pH will also increase the solubility of most anodic corrosion products and some cathodic inhibitor films. High flow velocity can also cause depolarization, promoting diffusion of ions or dissolved gases, both away from and to the metal surface. High velocity of water containing suspended material can erode a passive film from the metal surface. The net effect of depolarization is an increase in corrosion rate.

Passivity and Immunity

Immunity is the state in which a metal is more stable than oxides of that metal in a given environment. Metals that are immune to corrosion are called noble metals. Gold and platinum are examples of noble metals that are immune to corrosion in most normal environments.

Passivity is the state in which a metal forms a stable protective oxide layer on the surface, which prevents further dissolution of the metal. This passive oxide layer is formed by corrosion on a clean metal surface. The corrosion products are insoluble and rapidly form the passive film. The film acts as a barrier, separating the metal surface from the environment. For further corrosion to occur, the reactants must diffuse through the oxide film. Such diffusion is very slow or nonexistent, thus corrosion either markedly decreases or stops.

Passivity is essentially a condition on the metal surface where the corrosion rate is very low and a loss of chemical reactivity has occurred. Stainless steel is a good example of a metal that exhibits passivation in the presence of oxygen. The passive film is invisible and very thin, but significantly inhibits corrosion.

To be effective, a passive film must provide a barrier to both electron flow and diffusion of atoms and ions to and from the metal surface. An effective film must resist breakdown. The formation of a passive film is a dynamic process; the film can be broken down, and repassivation can occur. If the rate of breakdown exceeds the repassivation, corrosion can occur. If the breakdown is localized to small areas, pitting can occur. (Pitting corrosion is covered in more detail later in this chapter.)

Breakdown of the passive film can occur by chemical, electrochemical, or mechanical factors. Chloride ion in water can cause chemical breakdown of passive films. Mechanical breakdown can occur due to stress or abrasive wear, such as high-velocity water containing suspended solids. Inhibitor-created passive films can break down by these external factors, or by lack of program control. If the inhibitor level drops, passivation rates can decrease and corrosion rates increase.

Factors Influencing Corrosion

A number of parameters affect whether corrosion will occur, as well as the rate of corrosion itself. Adjusting system operation accordingly can significantly reduce corrosion. The more common and important factors will be discussed.

Water Chemistry

Water chemistry has a strong and varied effect on corrosion. The influence of dissolved solids on corrosivity is complex. The concentration and type of ion are both important. For example, some dissolved solids (carbonate and bicarbonate) reduce corrosion, while other aggressive ions (chloride and sulfate) typically increase corrosion by interfering with the protective film. Corrosivity does not increase at a linear rate with increasing total dissolved solids concentration (Fig. 16.8).

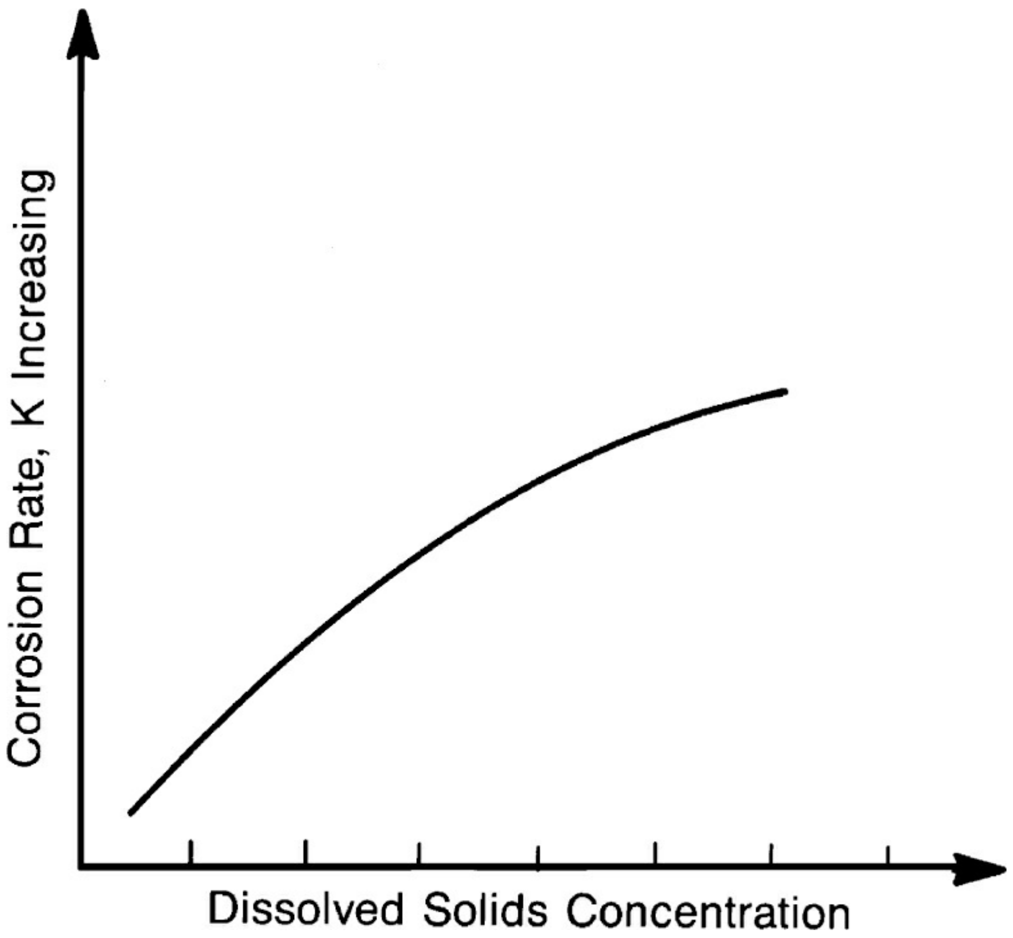
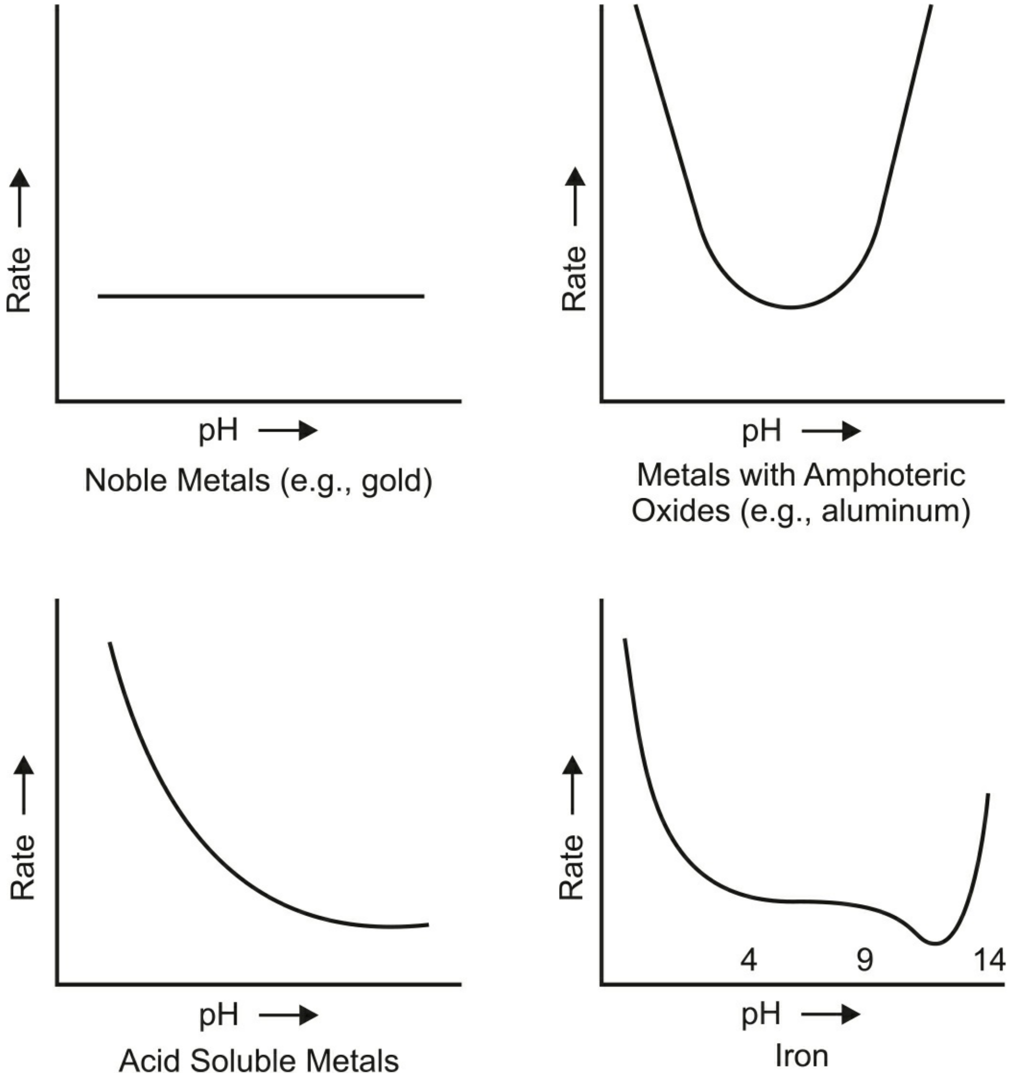


FIGURE 16.8 Influence of dissolved solids on corrosion rate.

Anything that increases solubility of the metal will increase corrosion. The pH of the water can have a dramatic effect on corrosion, and this effect varies with different metals. Figure 16.9 shows the effect of pH on four different metals. With most metals, acidic conditions are corrosive. The increase of hydrogen (H^+) in the water at low pH can dramatically increase the rate of the cathodic reaction, since H^+ is reduced at the cathode. The corrosion rate in acidic conditions will depend upon the alloy and the type of acid. For instance, oxidizing acids such as nitric will passivate stainless steel but will destroy carbon steel and yellow metals. Noble metals like gold will resist the corrosive effect of most acids. Amphoteric metals like aluminum and zinc corrode with both acid and base, and the corrosion rate increases at both ends of the pH spectrum. Chelating materials can increase corrosion on many metals by increasing the metal ion solubility.



Noble Metals (e.g., gold)

Metals with Amphoteric Oxides (e.g., aluminum)

Acid Soluble Metals

Iron

FIGURE 16.9 Variation in corrosion rate with pH for different metals.

Chloride and sulfate are aggressive ions that can increase corrosion rates. Chloride will attack the passive film on both steel and stainless steel. Chloride increases the solubility of ferrous ions and can prevent good film formation. Chloride ions play a strong role in ion concentration cells that can occur in crevices or under deposits, and chloride is a direct contributor to stress corrosion cracking of austenitic stainless steel. (Concentration cell corrosion and stress corrosion cracking are covered later in this chapter.) A key factor in diminishing the effect of chloride in cooling water systems is surface cleanliness. Minimizing deposition will help prevent ion concentration cell formation and allow the corrosion inhibitors to function more effectively, minimizing the impact of chloride on corrosion.

On the other hand, alkalinity in the water can have a very positive role in reducing corrosion. Alkalinity can reduce the rate of both the anodic and cathodic corrosion reactions. As an anodic inhibitor, alkalinity buffers the pH to regions where formation of ferrous hydroxide is favored. This ferrous hydroxide is an intermediate step to the formation of gamma iron oxide (FeOOH). Carbonate can participate in the anodic reaction by the formation of ferrous carbonate ion pairs in solution. These ferrous carbonate clusters can react with oxygen in solution to form gamma iron oxide under the right conditions. The reaction with oxygen is preferred, since the gamma iron oxide forms a passive film on the surface as shown in Fig. 16.10. Strongly passivating conditions result at pH around 9.0 to 9.2 under cooling system conditions. At lower pH, around 8.5, the system is not as strongly passivating. As a cathodic inhibitor, calcium carbonate can precipitate due to the locally higher pH at the cathode. This film can prevent the reduction of oxygen by preventing the electrons from migrating out of the metal. The formation of the cathodic film is dependent on the solubility of calcium carbonate in the system and at the surface. The solubility of calcium carbonate is a delicate balance, because too much precipitation will cause scale and too little calcium carbonate will allow corrosion to continue. Therefore, the anodic mechanism is more desirable for corrosion prevention.

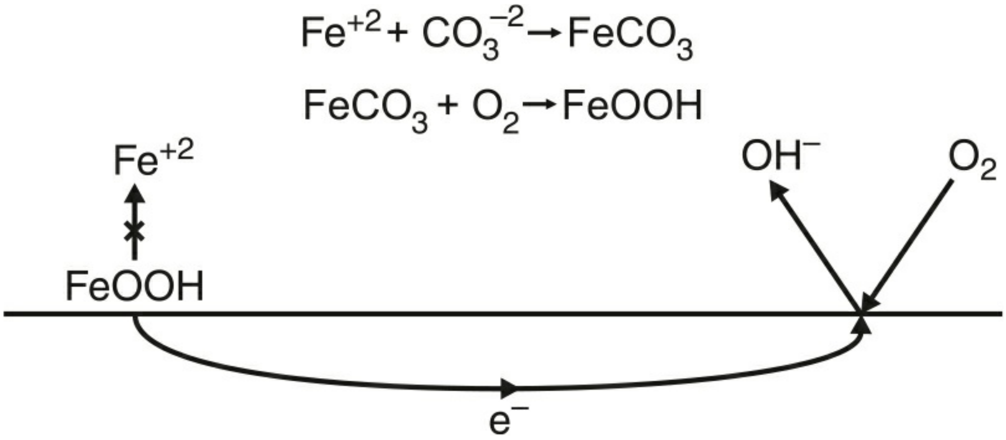


FIGURE 16.10 Alkalinity aids in the formation of gamma iron oxide.

Dissolved Gases

Carbon dioxide (CO_2) and dissolved oxygen (O_2) are the major gases of concern in cooling systems. Increasing the free CO_2 content in water reduces pH and increases corrosivity. In weakly buffered condensate in a steam system, this could produce low pH and corrosive water. However, in buffered water, like a typical cooling water system, the impact of the increased CO_2 is usually minimal. (Dissolved oxygen was covered earlier in this chapter.)

Hydrogen sulfide (H_2S) and ammonia (NH_3) are less frequently encountered gases, but both can increase corrosion of iron and copper alloys. Hydrogen sulfide is usually ionized as bisulfide and sulfide ions, which tend to depolarize the anodic area. Ammonia increases the corrosion rate of copper and copper alloys by forming soluble complexes with the copper. Ammonia can remove protective cuprous oxide or copper carbonate surface films.

Halogens and Other Oxidizers

Oxidizing agents, like chorine, can interfere with inhibiting films on metal surfaces. Oxidizers can act as depassivating agents by destroying a passive film on a metal surface. Halogens, particularly chlorine, can promote corrosion of copper and copper alloys. Chlorine can react with and strip the inhibitor film that may be created by azole-based copper corrosion inhibitors. The loss of the azole film will increase corrosion rates.

Temperature

As a rule, a temperature increase of 18°F (10°C) doubles the rate of most chemical reactions. Therefore, an increase in temperature increases the speed of corrosion, because the corrosion reactions proceed faster. In addition to increasing the rate of reactions, the oxygen diffusion rate also increases with increased temperature. Fig. 16.11 shows the relationship of temperature and oxygen concentration on corrosion rates.

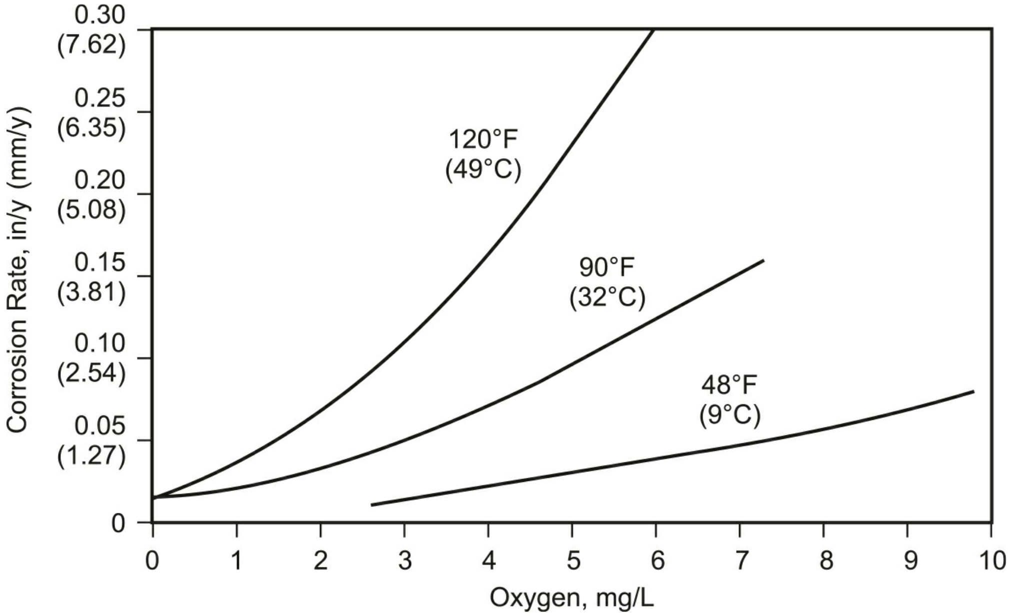


FIGURE 16.11 Effect of temperature on corrosion at different oxygen concentrations.

Flow Velocity

In general, corrosion will increase with an increase in water velocity, and corrosion normally becomes more uniform (general etch). However, the effect of flow velocity change is not always that simple. High and low flow rates can have both positive and negative effects on corrosion. Figure 16.12 depicts the general relationship between water velocity and the corrosion rate for steel.

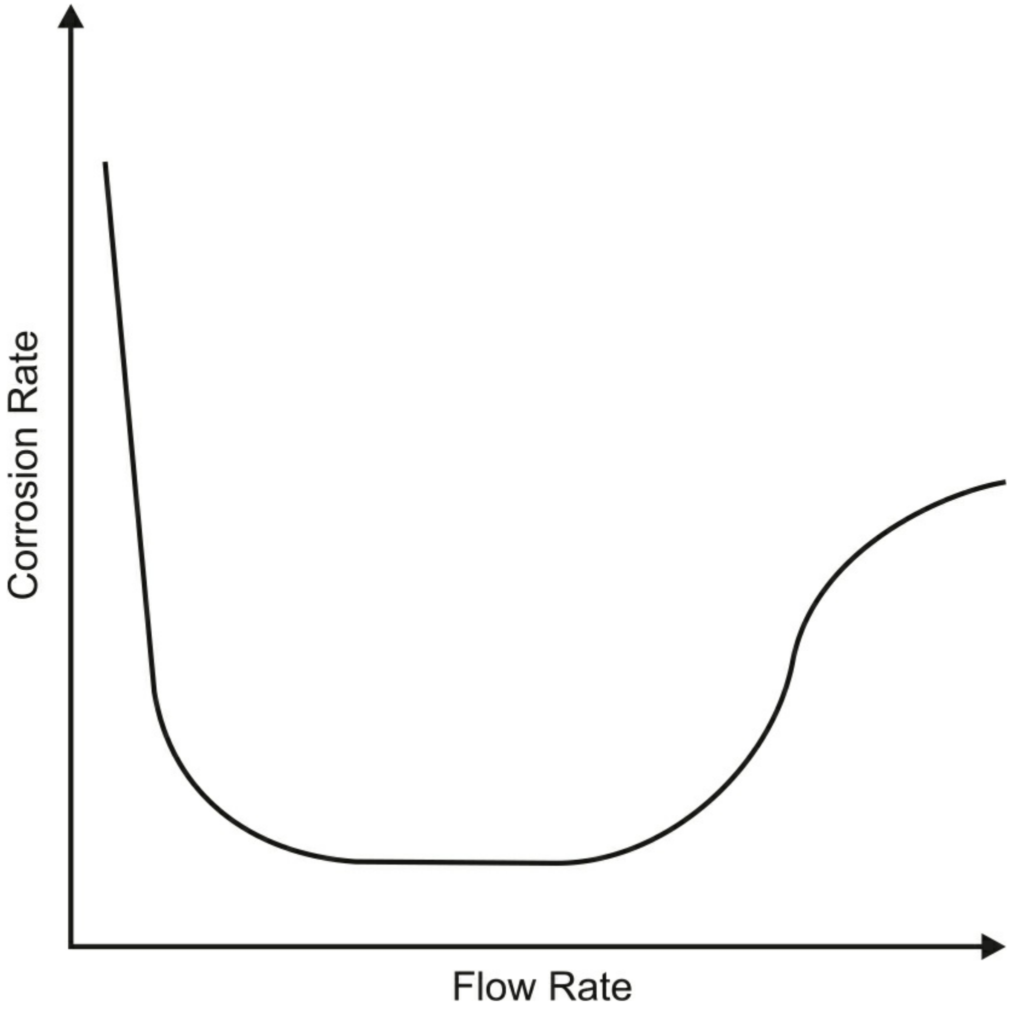


FIGURE 16.12 Both low and high water velocity can increase corrosion.

Examples of negative effects that relate to Fig. 16.12 include:

- Erosion corrosion can occur at very high water velocity.
- Oxygen is carried to cathodic sites more effectively at high water flow rate, increasing the cathodic reaction rate.
- Low flow or stagnant conditions allow suspended material to settle onto the bottom of tubing and bottom surfaces of other components. This promotes under-deposit corrosion.
- At low flow, iron oxide deposits are generally loose and nonprotective.
- Tubercle formation on iron is often more severe in low-flow situations. This is a form of under-deposit corrosion.

- Biocides and inhibitors will not be replenished as rapidly at the metal surface when low flow exists. Control of microbial growth and corrosion protection is reduced under low-flow conditions.

Positive effects of water velocity changes include:

- Increased velocity can decrease corrosion by replenishing corrosion inhibiting ions at the metal surface faster.
- Some metals and alloys, such as iron, aluminum, and stainless steel, rely upon oxygen to form a passive film that will inhibit corrosion. Increasing the water velocity will increase the oxygen supply available at anodic sites to speed the formation of protective oxide films.
- Proper water velocity and a good treatment program will help to keep metal surfaces clean, which aids corrosion inhibitor effectiveness and helps prevent under-deposit corrosion.

From a practical standpoint, the water velocity should be sufficient to keep the surfaces clean so that the corrosion inhibitors can function on the metal surface.

System or Spatial Configuration Factors

A variety of physical factors in the system can cause increased localized corrosion. Obviously, crevices created by poorly joined surfaces can lead to concentration cell corrosion, as discussed later in this chapter. Dead spaces or low-flow areas can create corrosion problems due to deposition, lower oxygen concentrations, or microbial growth that may exist in these areas. Places where water flow changes direction rapidly, or where a sudden pressure decrease occurs, can cause corrosion by erosion of the metal or the inhibiting film. Erosion corrosion is a process where the inhibiting film is repeatedly worn off and then reforms. This process eventually causes severe loss of metal thickness.

Deposits

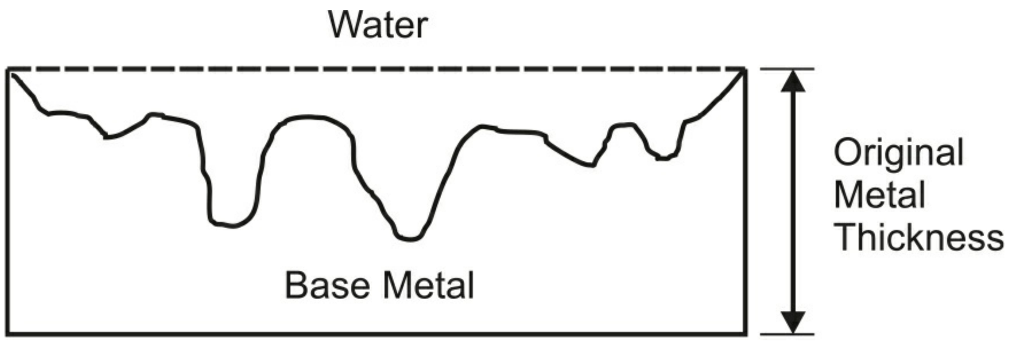
Most deposits generally have a negative effect on corrosion. Any type of deposit may cause under-deposit corrosion from the formation of differential oxygen or differential ion concentration cells. Deposits can harbor bacteria that can increase the deposition problem. Bacteria can influence corrosion directly by forming anaerobic environments for the growth of sulfate-reducing bacteria.

Types of Corrosion

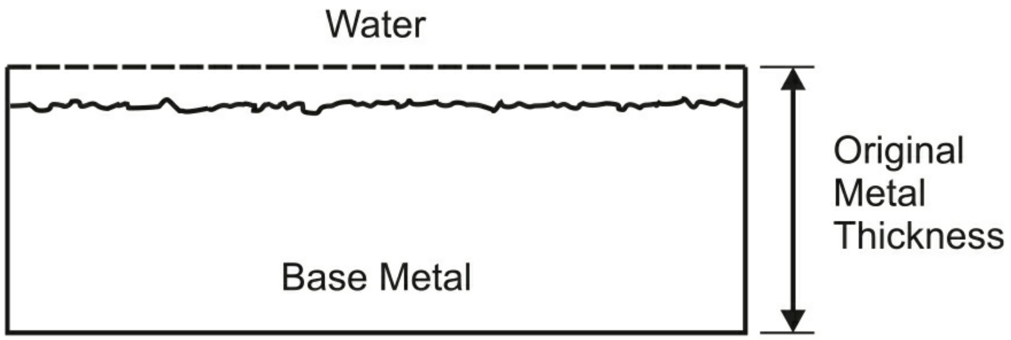
There is a variety of ways to classify the different forms of corrosion. Corrosion can be classified by appearance of the corroded metal, the area corroded, or the mechanism of the corrosion process. The most common forms of corrosion will be covered. More detail and additional examples of types of corrosion can be found in *The Nalco Guide to Cooling Water Systems Failure Analysis*, 2nd ed. mentioned earlier in this chapter.

Uniform Corrosion

Uniform or general corrosion happens when the anodic reaction (metal loss) occurs in a uniform manner on the metal surface. The anodic sites change location rapidly and are distributed over the metal surface. This type of corrosion loss is sometimes called general etch or general wastage, and is simply a progressive thinning of the metal (Fig. 16.13). In cooling systems, this form of corrosion may be experienced during an acidic pH excursion. The aggressive, acidic water will corrode the metal at all points on the surface, “etching” away the metal.



Localized / Pitting Attack



General Etch / Uniform Attack

FIGURE 16.13 Appearance of pitting and localized corrosion versus uniform corrosion.

General corrosion is the most common form of corrosion experienced in industry. The thickness of cooling system piping is designed for an expected general corrosion rate, dependent upon the desired service life. Uniform corrosion can be reduced by the proper application of corrosion inhibitors, coatings, or cathodic protection. Thus, this is the least dangerous and most easily prevented form of corrosion. General corrosion is the most predictable and easily measured with corrosion coupons or continuous monitoring devices. (See Chap. 18 on Cooling Water Monitoring.)

Pitting Corrosion

Pits are generally defined as a cavity or hole where the surface diameter is equal to or less than the depth of the pit. Pits can be distributed across a metal surface or isolated to a given area. Figure 16.13 compares pitting metal loss with uniform metal loss. Pitting corrosion is a common result of breakdown of a passive film in a small, localized area. This localized area becomes anodic, and the remainder of the inhibited surface of the metal is the cathode. The corrosion rate can be very high, when the anode is small and the cathode is large. This type of pitting can occur on clean surfaces as well as surfaces with deposits. For example, in some aggressive environments, pitting will occur on clean stainless steel surfaces. Pitting is more dangerous than general corrosion because pitting can proceed more rapidly and is focused on discrete areas. This can result in system metal failure much faster and with less overall metal loss than general corrosion.

Pitting can occur very quickly if a treatment program is not controlled properly. Low dosage of an anodic corrosion inhibitor like nitrite can cause breakdown of the passive film on metal surfaces. Pitting corrosion will result if the breakdown of the passive film is in small areas compared to the size of the remaining inhibited metal surface. The small areas are active anodes, and metal loss can proceed rapidly due to the large inhibited surface, which is the cathode. This is why oxidizing, anodic corrosion inhibitors are referred to as “dangerous inhibitors.” Control of dosage above a minimum value is essential to maintain the passive film.

Localized Corrosion

Localized corrosion can take many different forms that proceed by a variety of processes. Localized corrosion typically covers less than two-thirds of the metal surface. The most common forms in cooling water systems are tuberculation, under-deposit attack, and crevice corrosion. These types of localized corrosion are forms of concentration cell corrosion and all proceed by a similar mechanism, where the concentration of a given species in the water is different at the anode than at the cathode. The crevice or deposit helps to create and maintain the concentration difference. This illustrates the importance of treatment to both inhibit corrosion and keep the surfaces clean and free of deposits. Pitting may result from concentration cell corrosion that occurs under deposits, but localized corrosion sites may have larger openings than the depth of the corrosion site.

Concentration Cell Corrosion Mechanisms

If the concentration of a dissolved ion or molecule is different at two places on the metal surface, a concentration corrosion cell can occur. Surface deposits or crevices provide the conditions necessary for the formation of differential concentration cells. A crevice can form wherever two pieces of metal are joined. The crevice may be very small, even only a few thousandths of an inch (100 µm) wide, but this is large enough to fill the crevice with water for corrosion to occur. Surface deposits shield the metal from the bulk solution. Deposits on the metal surface or a crevice can create the conditions for concentration cell corrosion.

A variety of dissolved species can cause concentration cell corrosion:

- Dissolved oxygen
- Chloride or sulfate ions
- H^+ or OH^- ions (pH)

Since corrosion consumes oxygen in the under deposits or in a crevice, the concentration of oxygen in these locations will become lower than the oxygen concentration outside the deposit. Figure 16.14 shows the formation of a differential aeration cell under a deposit. The metal surface beneath the deposit becomes anodic, metal loss occurs, and a concentration corrosion cell is initiated. The anodic and cathodic reactions are the same reactions that occur in general corrosion, but here the two reactions are separated on the metal surface by deposits.

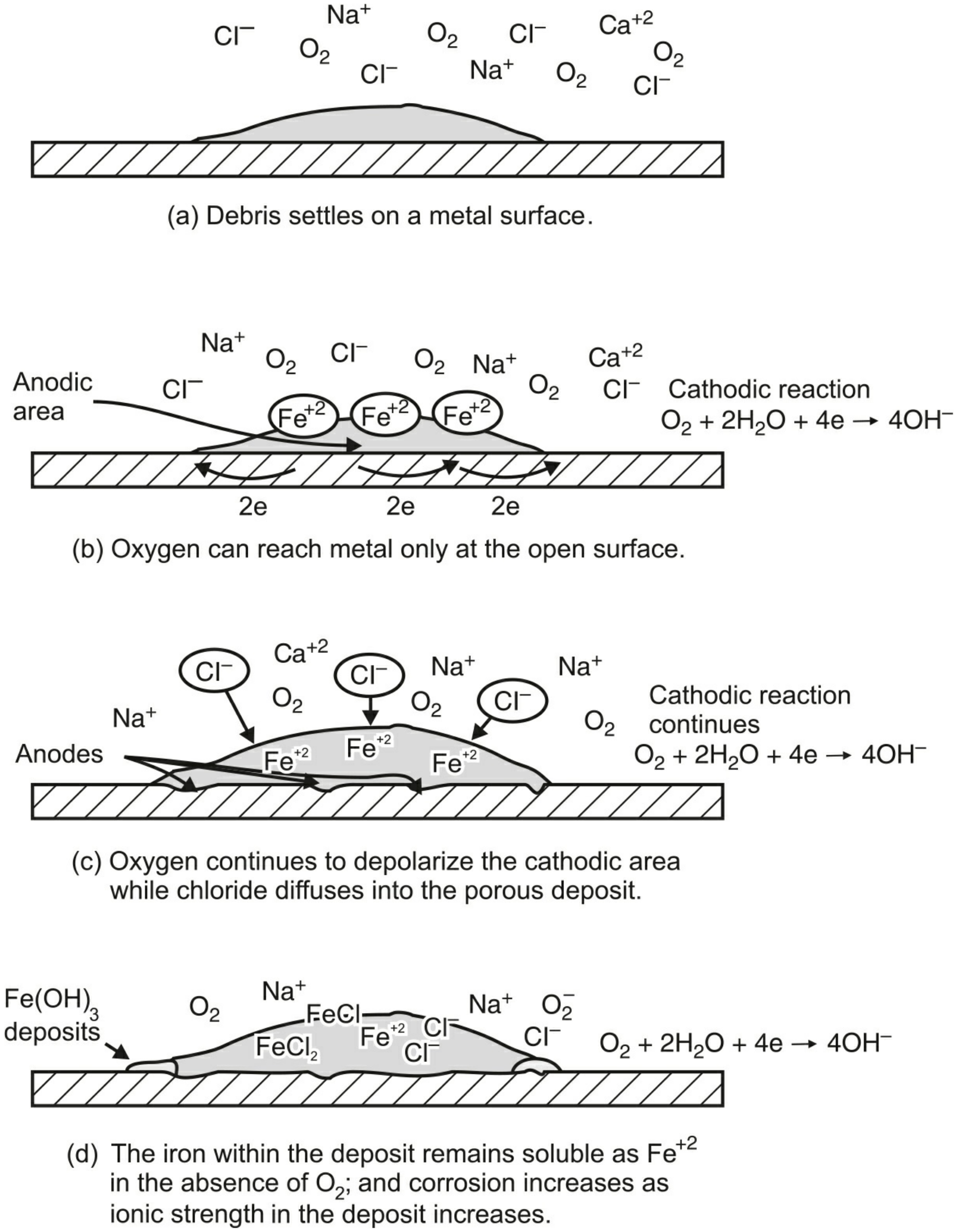


FIGURE 16.14 The sequence of steps in the formation of an oxygen concentration cell due to deposit on a steel surface in oxygenated water.

The corrosion under the deposit or in a crevice becomes progressively worse as metal ions are released into the solution at the anode. The solution at the anodic site takes on an excess positive charge. This positive charge will attract anions like chloride to maintain electroneutrality of the solution. If the deposit is semipermeable, this barrier inhibits the mixing of anodic and cathodic reaction products, but allows some species such as chloride and sulfate ions to pass through (Fig. 16.15). As the chloride and sulfate ions increase, more extreme corrosion can occur. Metal chlorides or sulfates can cause hydrolysis of water to produce acids under the deposits or in the crevice, further accelerating the attack. The crevice may become increasingly acidic as time progresses (pH around 3). The potential difference between the anode and cathode continues to increase, which will accelerate the corrosion rate. Thus, the conditions under the deposit can become autocatalytic and self-sustaining.

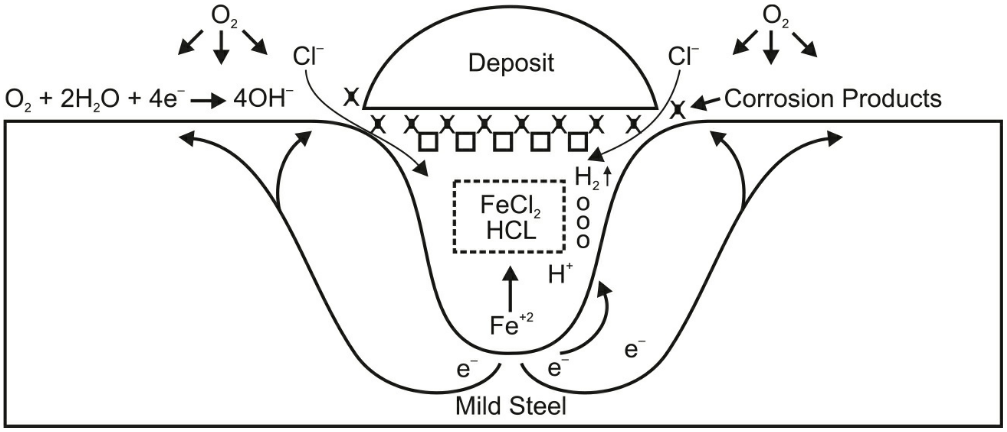


FIGURE 16.15 Chloride ion concentration cell under deposits can produce acidic conditions that accelerate corrosion.

In summary, deposits can aggravate localized attack, which starts as normal corrosion, but is compounded by various concentration cell corrosion mechanisms. Sometimes, microbial involvement may cause additional corrosion. The rate of differential concentration cell corrosion is proportional to the difference in concentration of the oxygen and ions under the deposit and the concentration of those species found in the water around the deposit. Because these concentration cells are shielded by deposits of corrosion products over the cell, not even the most effective corrosion inhibitors can get through to properly protect the metal surface. This emphasizes the importance of keeping water systems free of deposits.

Minimizing the concentrations of aggressive ions like chloride and sulfate by controlling concentration cycles can help to reduce concentration cell corrosion. However, this form of corrosion may occur as long as aggressive ions are present in the water. There is no safe limit for chloride and sulfate in solution, because these ions participate by a concentration mechanism. As the concentration of aggressive ions decreases, the severity of attack will decrease, but concentration cell corrosion can still occur at low chloride levels.

Tuberculation

Tuberculation is a unique type of under-deposit corrosion, where mounds of corrosion products cover localized regions of metal loss. Tubercles form on non-stainless steels and cast iron, when surfaces are exposed to oxygenated water. Soft water with high bicarbonate alkalinity stimulates tubercle formation, as do high concentrations of sulfate, chloride, and other aggressive anions. Tubercles can grow quite large and plug pipes, diminish water flow, and increase pumping costs. Tubercles cause localized corrosion, but generally do not cause pitting corrosion. The diameter of the corroded area is often much larger than the depth. In some cases, extensive tuberculation can appear like general corrosion after the surface is cleaned. In severe cases, tuberculation can cause penetration of the pipe or exchanger tube.

Corrosion under tubercles can occur by an oxygen concentration cell or by chloride and sulfate ion concentration cells that increase the anodic reaction rate. Anions can cause an acidic solution to form inside the tubercle, which helps to maintain the fluid-filled cavity. This is illustrated in Fig. 16.16. In addition, because of the reduced oxygen concentration and elevated sulfate levels, sulfate-reducing bacteria (SRB) can grow inside tubercles. This type of corrosion is rather common in systems that are not properly treated. Identifying tubercles is important so that corrective actions can be taken. Examples of tubercles in a water supply pipe and the damage tuberculation causes are shown in Figs. 16.17 and 16.18, respectively.

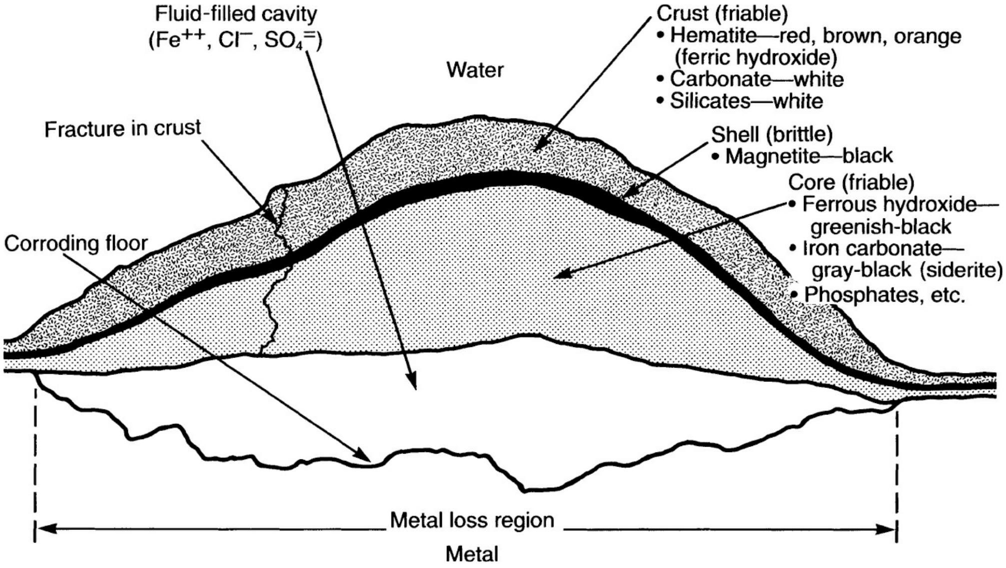


FIGURE 16.16 Cross section of a typical tubercle and the composition of the layers.

FIGURE 16.17 Example of tubercles that form long tubes in the direction of flow in a pipe.

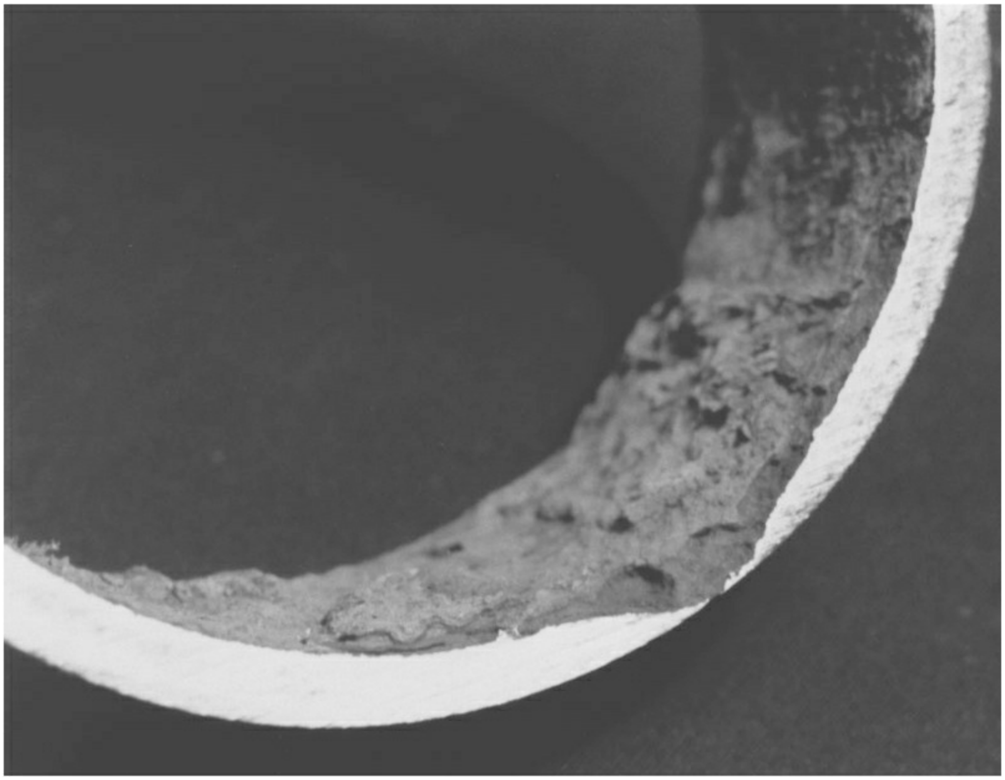


FIGURE 16.18 Example of a wide but deep corrosion site under a tubercle that actually penetrated this pipe.

Alloys

Under-deposit corrosion that occurs on alloys often involves differential concentration cells containing aggressive anions. The most common example is chloride concentration attack on stainless steel. The low pH that can occur in concentration cells under deposits will increase pitting or localized corrosion. The deposits can be silt, sand, oil, process leaks, biomass, scale precipitates, metal sulfides, or manganese dioxide. Deposits that are more water permeable will produce the most severe attack. Any location in a system can experience deposition. Areas with low or intermittent water flow, such as shell-side heat exchangers, service water systems, sumps, or exchanger head boxes, may be problem areas.

Concentration cells on stainless steel cause depassivation of the metal surface. The concentration of aggressive ions causes breaks in the passive surface, and corrosion attack can be intense and localized, as shown in Fig. 16.19. Loss of metal below the surface can be much greater than metal loss on the surface.

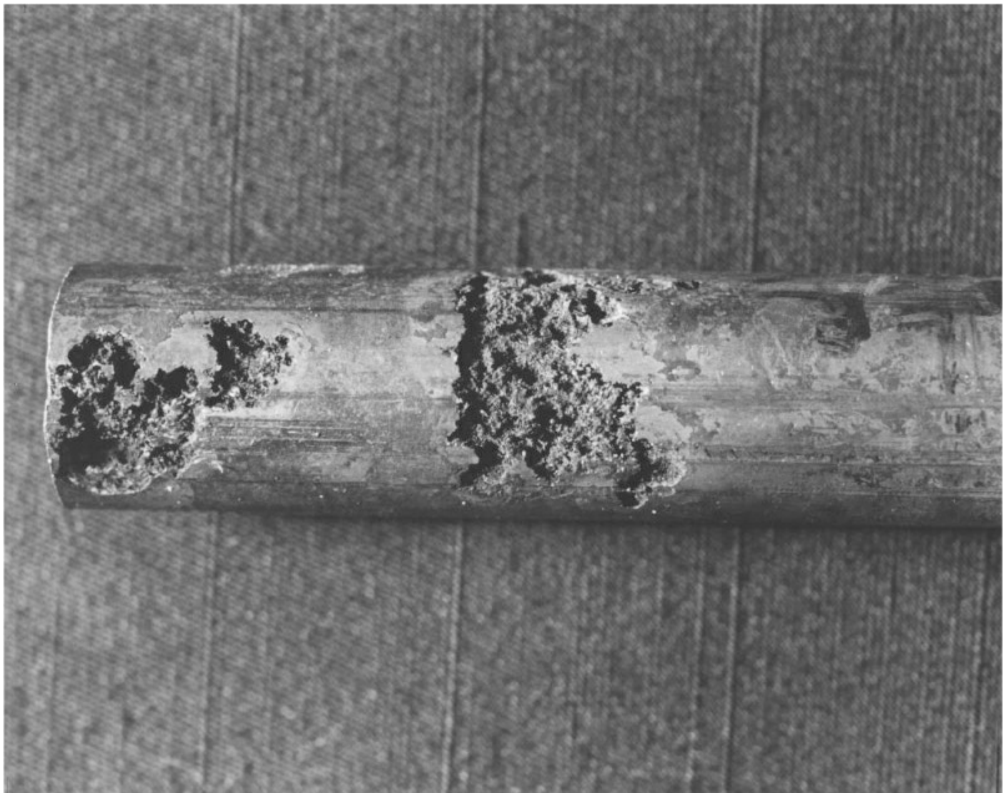


FIGURE 16.19 Example of severe localized corrosion in a 316 stainless steel heat exchanger tube that occurred under deposits on the tube surface.

In utility condensers that are made of copper alloys, pitting under manganese deposits can be a problem. This is particularly common in once-through condensers, where the supply water contains soluble manganese. Chlorination of the water or the action of dissolved oxygen can oxidize the manganese to insoluble forms that precipitate on the condenser tubing. Deposition in the condenser is increased when water is chlorinated immediately preceding the condenser inlet or water box. Manganese dioxide deposits are more noble than the tube metal, and promote corrosion due to galvanic effects (Fig. 16.20). This type of corrosion will occur on 304 stainless steel as well.

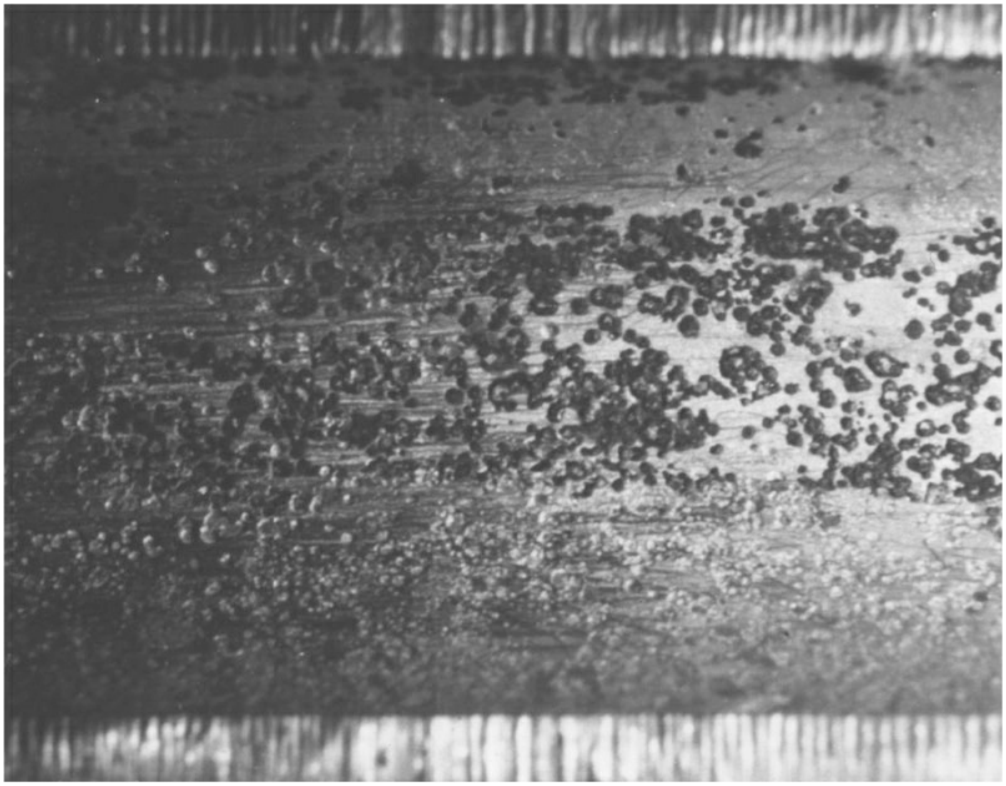


FIGURE 16.20 A 90:10 cupro-nickel condenser tube with small pits under the dark manganese-rich nodules on the surface.

Microbiologically Influenced Corrosion

Even the name of this type of corrosion has created controversy. Some think the corrosion is "induced" by the presence of biological organisms, while others think corrosion is only "influenced" by them. This is another "chicken and egg" situation. Either case may be correct depending on the organism and conditions. Microbiologically Influenced Corrosion (MIC) is now accepted to be corrosion that is either *actively induced* or *passively influenced* by microbial organisms.

Microorganisms can contribute to corrosion in different ways. In any case, the basic electrochemical corrosion reactions are still part of the process. Some microbial organisms will produce byproducts that actively accelerate corrosion or produce new corrosion sites. All microbial organisms can create deposits that form sites for under-deposit corrosion from concentration cell mechanisms. Pitting or localized corrosion is often a result of MIC. The interior of the corrosion site is usually hemispherical in shape and characteristically smooth, often with concentric rings on the metal surface. Pits are often more smooth on more corrosion-resistant metals. The metal surface beneath the corrosion products is often bright or shiny. Pits can also undercut the surface to give a characteristic profile when viewed in cross section, as in Fig. 16.21.

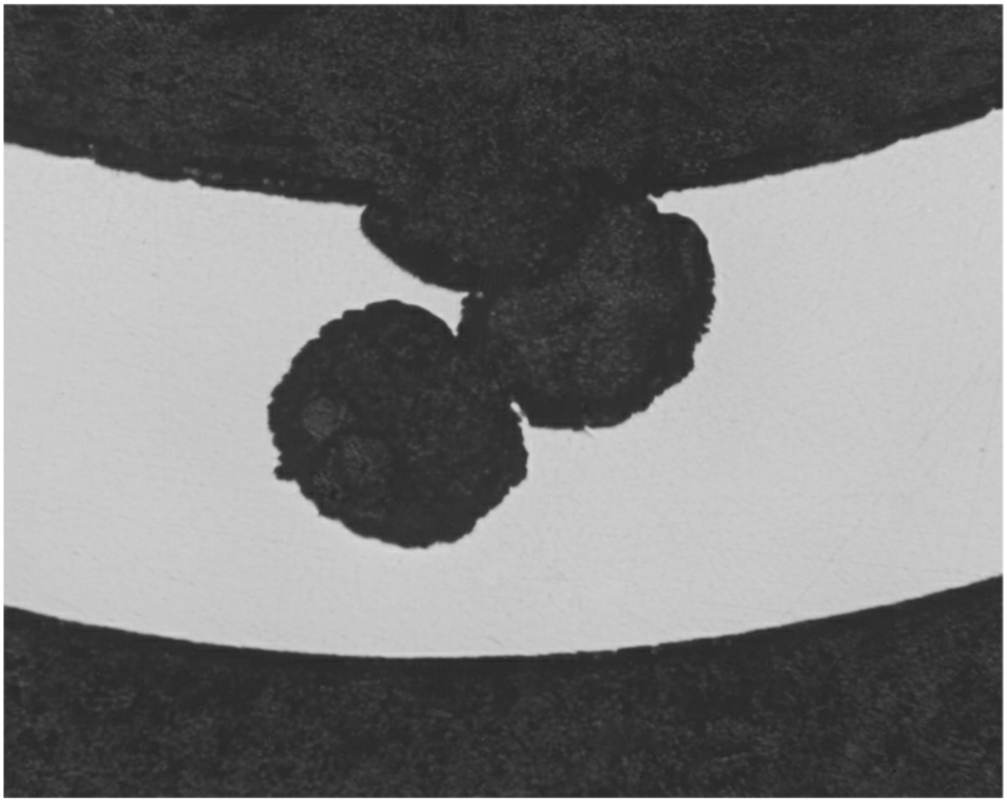


FIGURE 16.21 Example of pits caused by MIC that partially undercut the surface of a 316 stainless steel tube.

The key organisms that participate actively in corrosion fall into four main types: sulfate reducers, acid producers, metal depositors, and slime formers. The most common form of MIC involves SRB. These anaerobic bacteria grow in the absence of oxygen. SRB may survive when oxygen is present but do not actively grow. SRB occur in most natural waters and in soil or sediments. *Desulfovibrio*, *Desulfomonas*, and *Desulfotomaculum* are three common genera of sulfate reducers. Sulfate (SO_4^{-2}) or sulfite (SO_3^{-2}) must be present for them to actively grow. The metabolic process of these bacteria reduce sulfate to sulfide (S^{-2}). Because SRB are anaerobic bacteria, sulfate reducers will be found more predominately under deposits. SRB can be determined by microbial analysis. Corrosion sites are often filled with black corrosion products containing iron sulfides. If SRB are found in a recirculating water sample, this could mean larger quantities are present under deposits in the system, and indicate potential problems.

A variety of mechanisms has been proposed to explain how SRB organisms accelerate corrosion under anaerobic conditions:

- Direct depolarization of the cathodic surface by removal of molecular hydrogen.
- Precipitation of ferrous sulfide at the anode. Ferrous sulfide is highly cathodic to metallic iron, and creates a galvanic cell.
- Creation of a highly corrosive pH (possibly < 3) under deposits because of H_2S and other metabolic byproducts, typically organic acids.

Other bacteria can produce acid, either organic or inorganic. Regardless of form, the acid will reduce the pH, which accelerates corrosion. *Thiobacillus thiooxidans* and *Clostridium* are often linked to accelerated corrosion on steel. These are both anaerobic bacteria and survive best under deposits. *Thiobacillus* will oxidize sulfide to sulfate and may support the action of SRB deeper inside the tubercle. *Clostridia* produce short-chain organic acids that can be quite aggressive to steel.

Metal-depositing bacteria can oxidize ferrous iron to ferric iron, producing ferric hydroxide in normal cooling water conditions. Some can also oxidize manganese deposits. The ferric hydroxide produces a loose, poorly protective deposit that creates conditions for under-deposit corrosion and tuberculation. *Gallionella* and *Sphaerotilus* are two forms of these bacteria.

Most slime forming bacteria produce secretions of extracellular polymers and other metabolic by-products. The slime layers can contribute to corrosion both actively and passively. First, the bacteria consume oxygen, creating conditions for differential aeration cells. The slime layers form an occluding deposit that can contribute to both differential aeration and differential ion concentration cells. These deposits can also provide sites for anaerobic bacteria to live under the slime layer.

Stress Corrosion Cracking

Very small cracks can form in metal under stress that is exposed to a specific corrosive species, like chloride. This failure is called stress corrosion cracking (SCC). Both stress and corrosion processes are necessary and critical factors for SCC to occur. These two processes interact synergistically to produce cracks in the metal. The cracks start on the surface and grow in response to the stress and perpendicular to the direction of the stress. The cracks may be longitudinal along the length of the pipe or transverse around the pipe circumference. Examples are shown in Figs. 16.22 to 16.24.

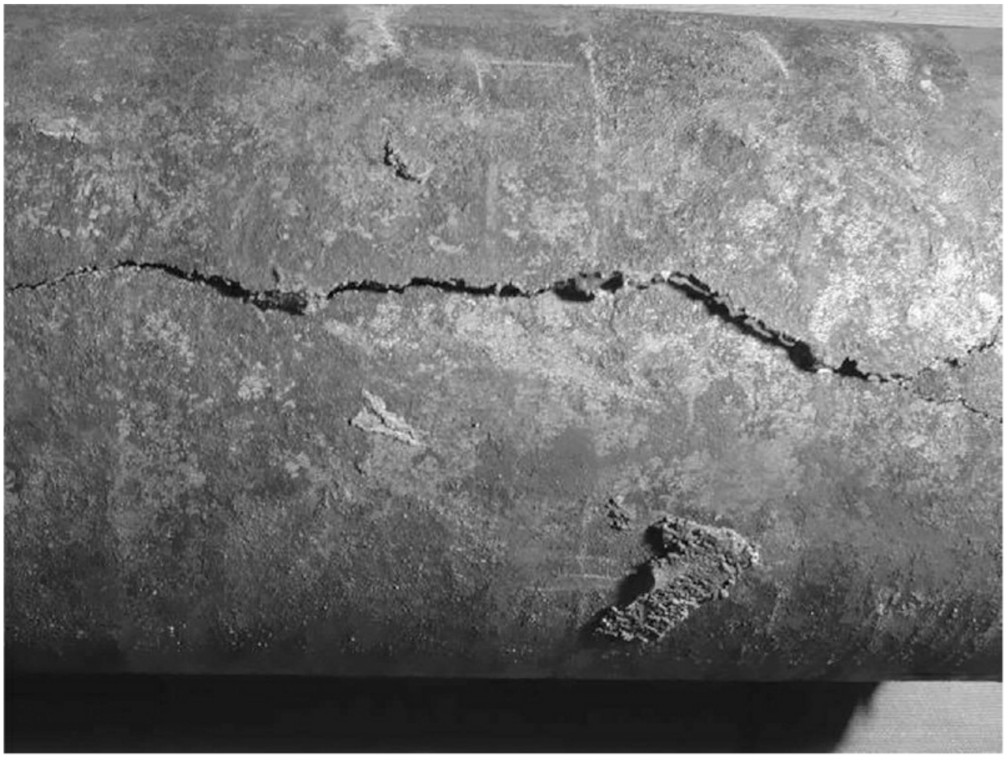


FIGURE 16.22 Example of stress corrosion cracking on stainless steel—longitudinal crack.

FIGURE 16.23 Example of stress corrosion cracking on stainless steel—transverse crack.

FIGURE 16.24 Example of severe stress corrosion cracking on a stainless steel pipe.

The first critical factor necessary for SCC to occur is a stress in the metal. An externally applied tensile stress or a residual stress from the manufacturing process can promote SCC. Examples include stress from thermal expansion or contraction, pressure, and service loads. Internal, residual stresses may be locked into the metal during fabrication by rolling, drawing, shaping, welding, or installation.

The second critical factor for SCC is the presence of a specific corrodent species in the water. A given alloy will be susceptible to SCC only when a specific corrodent is present. Stainless steel (300 series) will crack when exposed to chloride but not in the presence of ammonia. Figure 16.25 shows the nature of a stress crack in stainless steel exposed to water containing chloride. Brasses will crack in the presence of ammonia but not with chloride. In some cases, the concentration may not need to be very high, but in others, very high concentrations may be required.

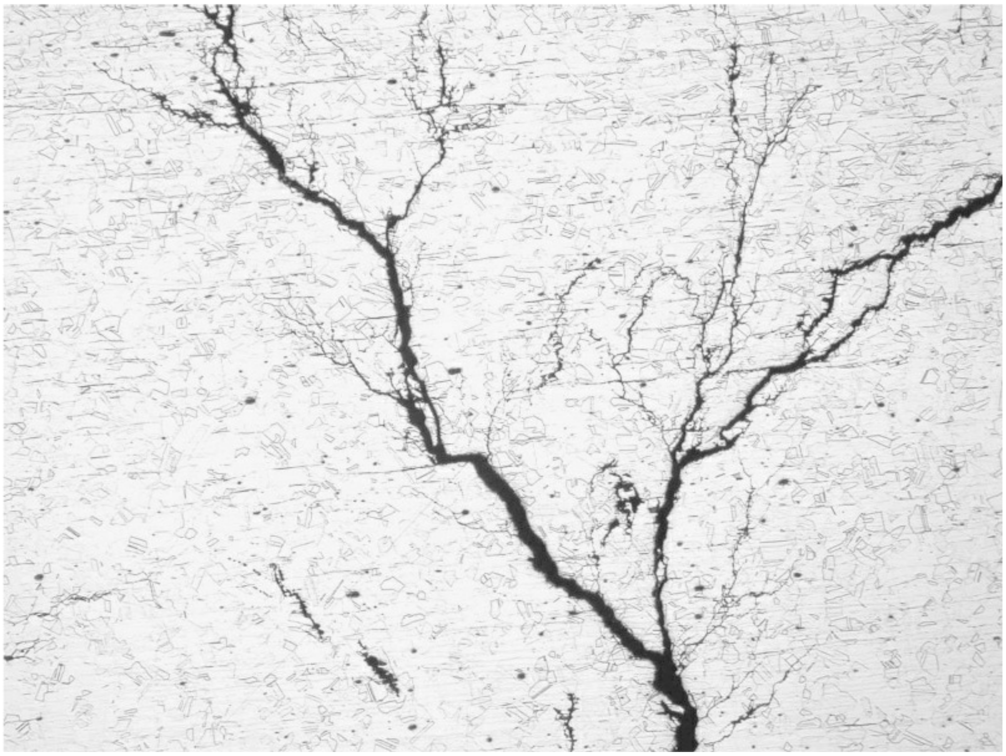


FIGURE 16.25 Stress corrosion cracking showing the typical branching of the crack.

SCC can be influenced by flow, alloy composition, concentration of corrodent, temperature, time, pH, presence of oxidizing agents, and the presence of deposits or crevices, which may concentrate corrosive agents. SCC can occur in a continuum from a high stress in a mildly corrosive environment to a mild stress in a highly corrosive environment, depending on all of the factors involved. Certain alloys have a temperature requirement for cracking to occur.

Largely, proper design and good fabrication procedures should produce equipment, piping, or structures free of internal stresses. For example, heat treatment after fabrication (stress relief annealing) allows the crystalline structure of the metal to free itself of internal stresses. Even large process vessels may be stress relieved to guard against stress corrosion cracking.

Much has been discussed about the concentration of the corrodent in recent years. SCC can occur at concentrations of specific corrodents of 10 mg/L or less, depending on the temperature. A concentrating mechanism may increase the rate or tendency for SCC, but the concentrating mechanism is not necessary for SCC to occur. The inability to accurately estimate the concentration of a corrodent needed for SCC is a key reason predicting SCC is difficult.

[1] The World Corrosion Organization, 2016, http://corrosion.org/

[2] Dillon, J., Desch, P., Lai, T., *The Nalco Guide to Cooling Water Systems Failure Analysis*, 2nd ed, Ed Flynn, D., McGraw-Hill, 2015.

CHAPTER 17

Cooling Water Biology

Bacteria are everywhere around us, in the water, air, and soil. Our bodies contain a wide variety of bacteria, some of which are useful, some are harmful, and some are just "along for the ride." If the bacterial population changes or grows out of normal proportion, the result is an infection. Just like our bodies, cooling systems are an ideal environment for bacterial growth. However, the cooling system can do nothing to control bacterial population growth without intervention by those who control the system. Therefore, the types of organisms that grow in cooling water systems and the impact of the growth and multiplication of the organisms must be understood to maintain proper system performance.

Microbial fouling is a central problem in cooling water systems (Fig. 17.1). Central because microbial slime can cause fouling from suspended material, corrosion, and scale formation faster than many other conditions in cooling water systems. Cooling water systems can be plagued with a variety of biological organisms. Bacterial slimes and algae come to mind first, because they are seen when heat exchangers are opened or on the deck of a cooling tower. Algae can also be a problem in large impounded lakes used for electric utility plant cooling. Other microorganisms like fungi or protozoa are sometimes found in cooling systems. Pathogenic organisms like *Legionella* bacteria can also be a problem. Finally, larger organisms like clams and mussels can cause macrofouling of once-through cooling water systems or pump intakes on lakes or rivers. This chapter will cover microbial fouling and macrofouling. *Legionella* will be covered in Chap. 20. Control methods to minimize biological growth in cooling water systems are covered in Chap. 19.

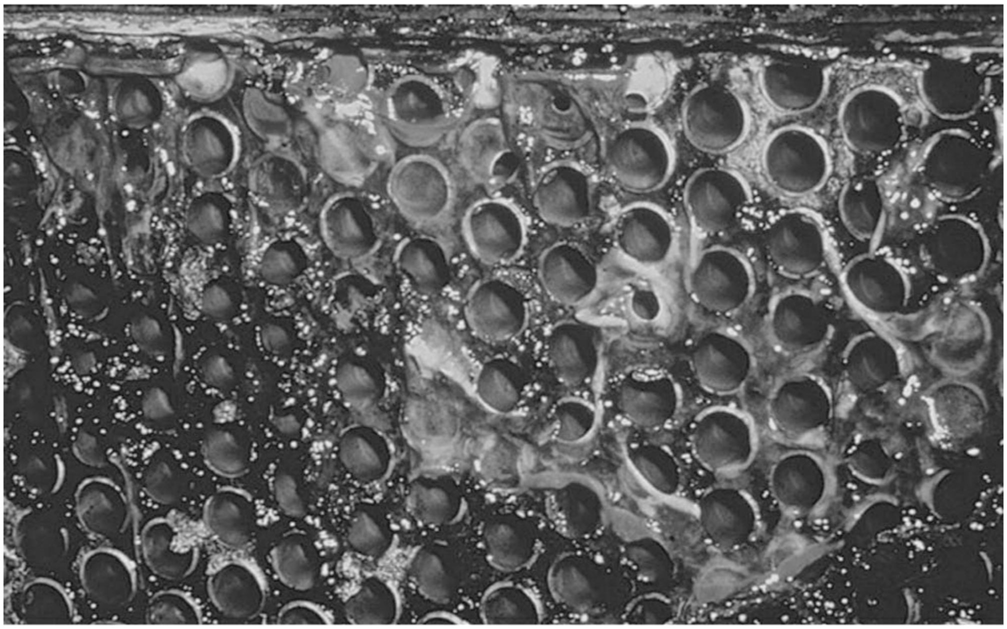


FIGURE 17.1 Bacterial slime on an exchanger tube sheet.

Sources of Biological Problems in Cooling Water Systems

Microorganisms enter cooling water systems from two primary sources. One is the makeup water in which microorganisms are already present. The concentration of organisms will vary depending on the source of makeup water. A river or lake may contain large amounts of biological growth, depending on the condition of that water source. A potable water source should have a very low bacterial population, but is not sterile. Some freshwater or salt-water sources may contain clams, mussels, or other macroscopic organisms that can grow in cooling systems and cause serious problems. The second source is via airborne microorganisms that are blown into the cooling tower. Windblown dust from soil or other dirt will contain a variety of organisms. Bacteria that can form dormant cysts or spores, will survive stressful environmental or very dry conditions then revive and grow once they are in a suitable environment. So the presence of biological organisms cannot be prevented, but the growth and subsequent cooling system problems caused by biofouling must be controlled to a level where problems do not occur.

Consequences

The consequences of biological growth in cooling systems are varied, depending on the type of organism and system involved. Heat transfer loss by bacterial slime in heat exchangers is the first consideration. Microbial slime, like other fouling materials, reduces the efficiency of heat transfer. In fact, microbial slime is more insulating than other common deposits (Fig. 17.2). Heat transfer reduction can limit the efficiency of a process, affect the quality of the product, cause increased maintenance cost, or even shut down a process.

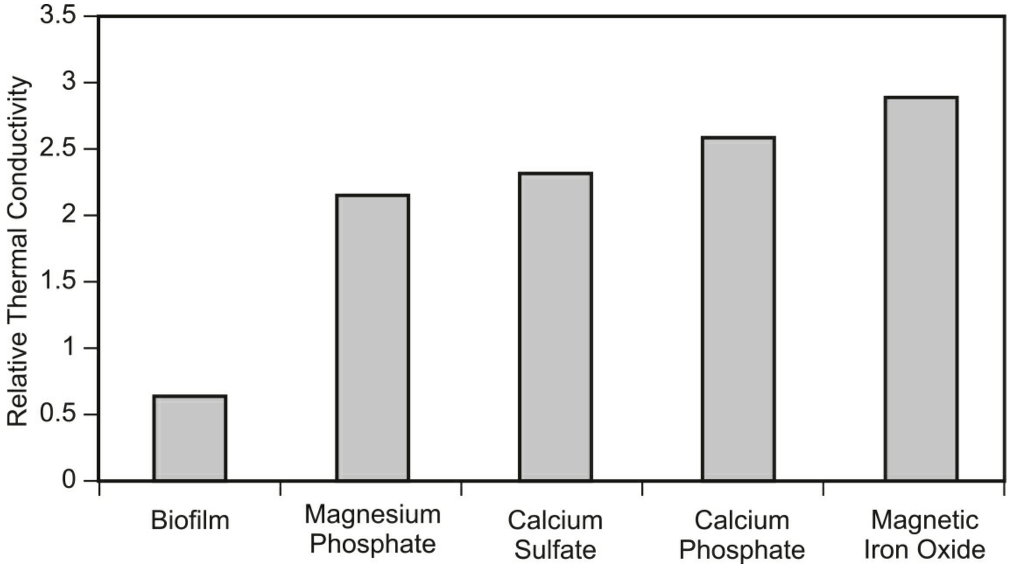


FIGURE 17.2 Biofilms have much lower thermal conductivity than other types of heat exchanger deposits.[1]

Another critical problem of biofouling is under-deposit corrosion. Certain organisms, for example sulfate-reducing bacteria, generate corrosive hydrogen sulfide, which can cause severe pitting on metal surfaces (Fig. 17.3). Slime can accelerate corrosion by depositing on the metal and preventing protective film formation. In addition, slime layers can also cause under-deposit corrosion by the formation of concentration cell corrosion. (See Chap. 16 on Corrosion for more information on concentration cell corrosion.) These problems can lead to penetration of heat exchangers, causing product contamination or increased fouling by loss of product into the cooling water.

FIGURE 17.3 A pit caused by sulfate-reducing bacteria that perforated a carbon steel pipe at a weld-backing ring.

Other problems include a reduction of tower performance from plugged water distribution nozzles on the deck of a cooling tower by algae. Flow reduction in pipes can be caused by bacterial fouling and can be a critical problem resulting from macrofouling in once-through cooling or in water intakes on oceans, lakes, or rivers. Larger organisms like clams and mussels cause macrofouling. The costs of macrofouling are estimated to be in the billions of dollars worldwide due to the high cost of either treatment or mechanical removal. Finally, material degradation, such as fungal deterioration of wood in cooling towers can cause serious structural or performance problems.

The sticky slime formed by bacterial deposits can trap other deposits, making the deposition problem worse. Slime masses provide excellent sites for the deposition of other foulants. Other microorganisms and suspended solids can add to existing fouling deposit. Slime on heat exchangers can cause or accelerate the rate of scale formation. When deposits form, heat transfer is reduced, and surface temperature increases. This temperature increase can result in precipitation of inversely soluble minerals like calcium carbonate or calcium phosphate. Bacteria can degrade some treatment chemicals, rendering them ineffective. If an inhibitor is degraded by microbial digestion, this could result in scale formation or corrosion. This causes possible production cutbacks and higher energy cost. This is why microbial fouling is placed at the center of the triangle representing the connection between the four problems of cooling water systems—corrosion, scale, fouling, and microbial growth. (See Fig. 15.1 in Chap. 15.)

Microorganisms Found in Cooling Systems

Bacteria, fungi, algae, and protozoa are the most common microorganisms found in cooling systems. Table 17.1 gives an overview of common organisms in these four groups. These organisms are the ones frequently associated with problems in cooling water systems. The classification is not strictly based on the biological classifications like order, family, genus, and species, etc., but combines this with metabolic processes of the organisms, and the types of problems that the organisms cause.

Classifications	**Description**	**Common Problems**
Bacteria		
Aerobic slime-forming *Pseudomonas* Pigmented Mucoids *Enterobacter* *Spores*	Sticky, gooey, masses usually colored by suspended solids or corrosion products.	Fouling Produce conditions for growth of anaerobic corrosive bacteria Produce acids Reduce heat transfer efficiency
Anaerobic corrosive *Desulfovibrio* *Clostridium* Facultative	Black appearance. Rotten egg odor (H_2S). Grow best under slime or other deposits and in low-flow areas.	Corrosion pH reduction
Iron-depositing *Sphaerotilus* *Gallionella*	*Sphaerotilus* can be white or rust-colored, whereas *Gallionella* is always rusty. Stringy, slippery; often forms voluminous red deposits.	Insoluble iron deposits Under-deposit corrosion
Nitrifiers	Produce acids in systems contaminated with NH_3.	pH reduction Corrosion due to inhibitor depletion
Fungi		
Molds *Aspergillus* *Penicillium* *Trichoderma*	Stringy, gooey, masses typically on wooden areas. Usually white or colored by system contamination.	Wood decay and fouling
Yeast *Torula* *Rhodotorula*	Leathery or rubbery; resembling mucus.	Fouling
Algae		
Oscillatoria *Chlorococcus*	Found living only in sunlight or source of light. Loose, slimy, rubbery. Often green or brown.	Plugging of distribution deck holes Food for slime-forming bacteria

Protozoa		
Amoeba Ciliates	Larger, single cell organisms, up to 0.04 mils (1 mm). Move under own power. Use bacteria, algae, and organic matter as food. Some can form cysts.	Usually indicate severe microbial contamination in system. Certain protozoa can host *Legionella* bacteria.

TABLE 17.1 Typical Microorganisms That Can Be Found in Cooling Systems and the Problems Associated with Them

The presence of many different types of organisms in a system is a sign that the system is hospitable to growth. Diversity is an indication that a system may be out of control, as many microorganisms thrive on the by-products of others. As total disinfection is usually not possible, a key concept in microbiological control is to manage the system to reasonable microorganism levels and minimize the diversity.

Bacteria

Bacteria, the largest group of troublesome organisms, cause the most varied problems. Nalco groups bacteria commonly isolated from cooling water systems into four classes: aerobic slime formers, anaerobic corrosive bacteria, iron-depositing bacteria, and nitrifiers/denitrifiers. Table 17.1 lists the bacteria, in addition to other organisms, normally encountered in cooling water systems. These microorganisms have been selected for discussion because they are the ones frequently associated with problems in cooling systems. Each group has its preferred environment and thrives in specific areas of a water system.

Aerobic Bacteria

A wide variety of aerobic bacteria commonly is found in cooling water systems. These bacteria require oxygen, so they are found in aerated waters in most cooling systems. These bacteria are metabolically diverse and can adapt rapidly to conditions, so that they can grow anywhere in the system. The most troublesome aerobes often are those that produce slime layers (Fig. 17.4). Cell walls in many microorganisms are covered with extracellular polysaccharide. In some cases, microorganisms are capable of producing large amounts of extracellular polysaccharides resulting in slimy deposits. These slime-encased cells attach to the available surfaces, reproduce, form additional slime, and develop into bio-deposits or biofilms. Biofilm formation and problems are discussed later in this chapter. The most common slime formers in cooling water systems are *Pseudomonas*, Pigmented, Mucoids, and *Aerobacter*. Of these, *Pseudomonas* is usually the most troublesome.

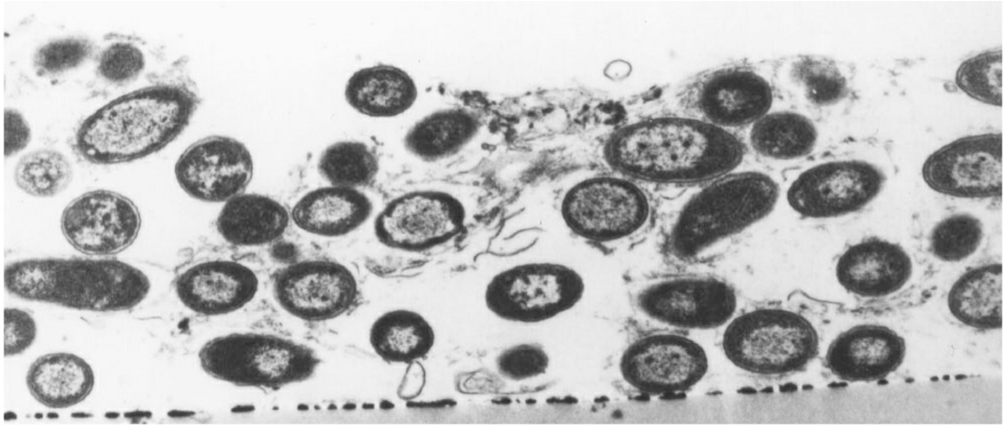


FIGURE 17.4 Example of biofilm. The bacterial cells are separated by the extracellular polymer that forms the slime that helps them stick to surfaces. Organisms are *Pseudomonas aeruginosa* at 7000×.

Some bacteria can be more harmful or indicate problems in cooling systems. *Enterobacter* is a type of coliform bacteria that is commonly found in sewage, and presence of *Enterobacter* in cooling water systems can indicate wastewater entering the system. *Legionella* bacteria are a potential threat to the health of individuals near a cooling tower. Chapter 20 covers *Legionella* in greater depth.

Anaerobic Corrosive Bacteria

Anaerobic bacteria are commonly found in both open and closed cooling water systems. Anaerobic bacteria do not require oxygen and obtain energy from reactions other than the oxidation of organic substances. Since anaerobes do not need oxygen, they are found in oxygen-deficient areas, such as under deposits, in crevices, and in sludge in tower basins. Several types of anaerobic bacteria cause corrosion of metal surfaces, such as sulfate-reducing bacteria (SRB). They obtain energy by reducing the ever-present sulfate ion to hydrogen sulfide (H_2S), a corrosive gas when dissolved in water. Some anaerobic bacteria produce organic acids as by-products of growth. These acids can also cause corrosion of some metal surfaces in cooling systems.

Desulfovibrio is the most notorious species of the sulfate-reducing bacteria. These organisms are widely found in wells, rivers, lakes, marsh soil, and in general, anywhere anaerobic conditions exist. *Desulfovibrio* require an oxygen-free environment to thrive. *Desulfovibrio* can survive for extended periods in a semi-dormant stage in the presence of oxygen. This allows them to move out of anaerobic environments and find new locations to inhabit. Other anaerobes such as *Clostridia* and facultative bacteria (those that can grow either with or without oxygen) also generate hydrogen sulfide from organic sulfur sources such as decaying algae.

The specific ways that SRB affect corrosion processes were covered in Chap. 16 (Cooling System Corrosion). The net effect is either initiation or acceleration of pitting corrosion on most metal surfaces, such as mild steel, aluminum, and stainless steel. Corrosion attributed to these anaerobes is always manifested as localized corrosion or pitting. The corrosion can cause penetration of the metal if allowed to proceed. Evidence of sulfate reducers is the unique, hemispherical pit etched on the metal surface, sometimes in the form of concentric rings (Fig. 17.5). Black deposits of iron sulfide in the bottom of the pits are also evidence of sulfate-reducing bacteria.

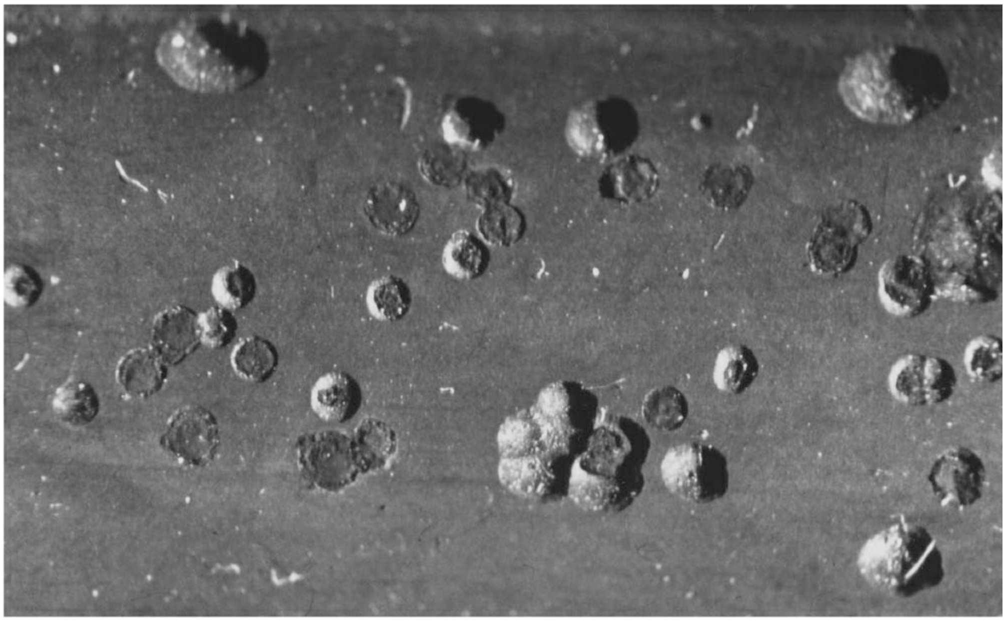


FIGURE 17.5 Smooth, hemispherical pits, often found in clusters or concentric rings are characteristic of sulfate-reducing bacteria.

Iron-Depositing Bacteria

These bacteria occur in water high in soluble, ferrous iron (Fe^{+2}), such as ground water, or beneath deposits on corroding iron or steel. Iron depositors convert ferrous ions to insoluble ferric hydroxide or oxide, which becomes part of the slimy, sticky sheath around the cell. These bacteria form deposits and accelerate corrosion rates, which produce additional soluble iron, further increasing the population of iron depositors in the system (Fig. 17.6).

FIGURE 17.6 Iron-depositing bacteria within tubercles contributed to the voluminous iron oxide deposition in this steel distribution pipe.

Two important species of iron-depositing bacteria in cooling water are *Gallionella* and *Sphaerotilus*. Both species can use soluble iron as an energy source. These microorganisms can live under low oxygen conditions or at interfaces between anaerobic and aerobic conditions. The iron deposits created by iron-depositing bacteria cause fouling and concentration-cell corrosion, as well as conditions under which anaerobic bacteria flourish.

Gallionella grow best in low oxygen conditions, for example, in water wells. These are environments where ferrous iron is not susceptible to chemical oxidation at neutral pH as occurs in aerated waters. *Gallionella* can use only soluble iron as an energy source, and the iron oxide formed is deposited within an outer sheath that has a spiral appearance when observed under the microscope (Fig. 17.7). The sheath containing the iron oxide then tends to deposit as a foulant in cooling water systems.

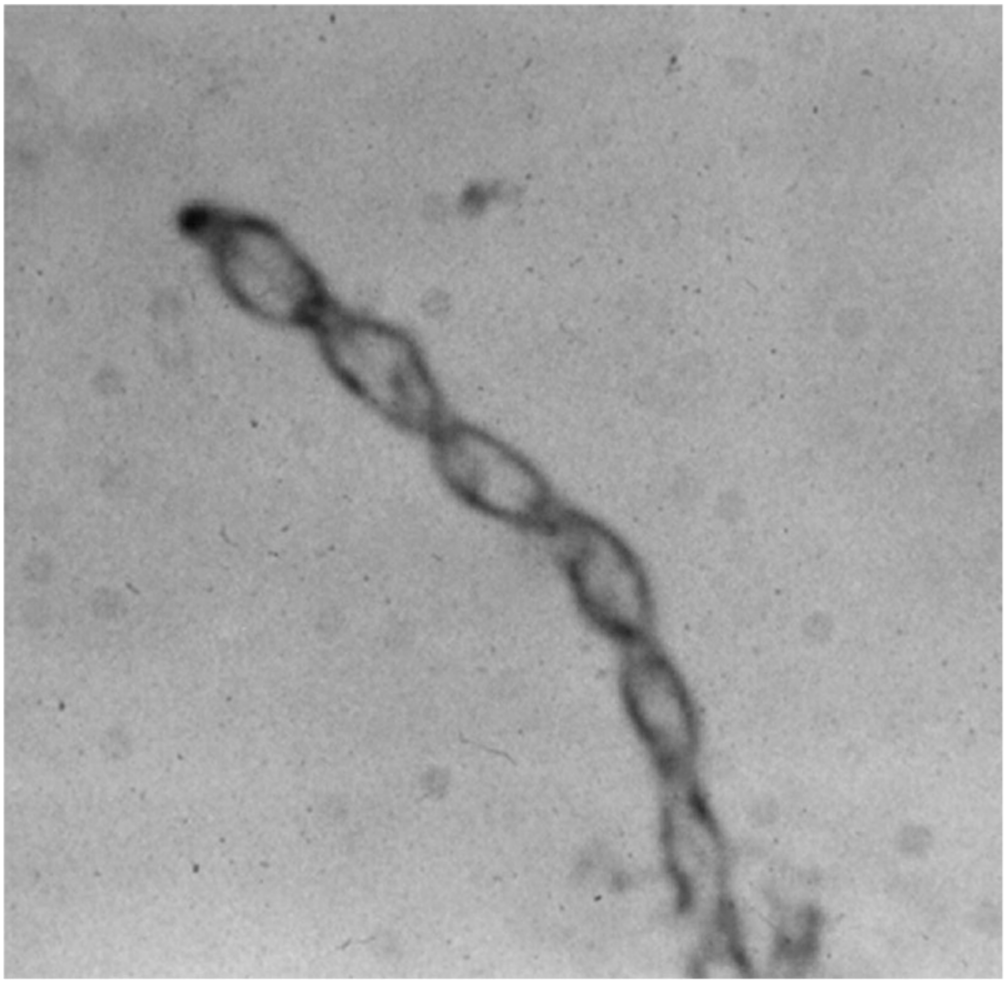


FIGURE 17.7 *Gallionella* are one type of iron-depositing bacteria (1000×).

Sphaerotilus can use either organic nutrients or ferrous ion as an energy source. The effect of these bacteria on cooling water systems differs slightly from *Gallionella* because iron is not always present in deposits formed by *Sphaerotilus*. In these instances, *Sphaerotilus* will be white. *Sphaerotilus* has a distinct microscopic morphology, as shown in Fig. 17.8. The cells look like a row of train cars and are found primarily in once-through systems. Since *Sphaerotilus* and *Gallionella* grow best in low oxygen environments, these two bacteria are not often found in open recirculating cooling systems.

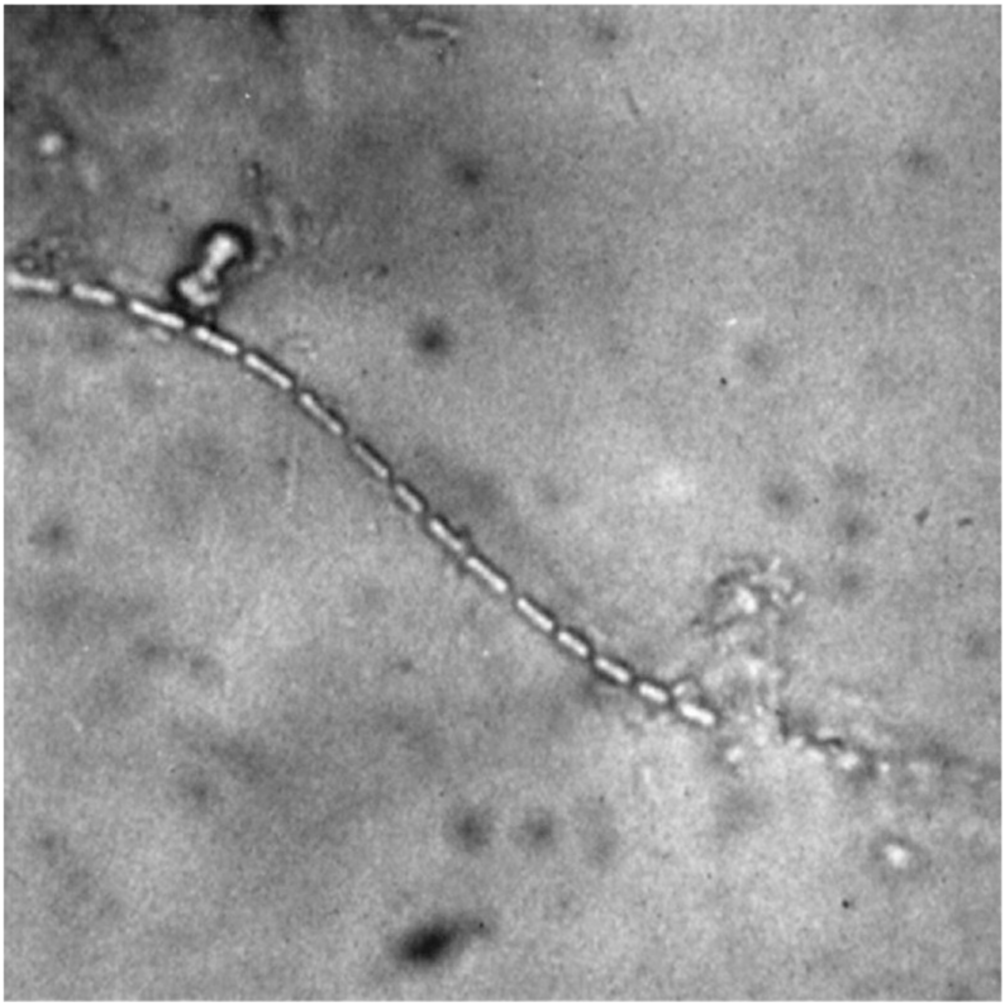


FIGURE 17.8 *Sphaerotilus* are another type of iron-depositing bacteria (400×).

Nitrifiers/Denitrifiers

Bacteria capable of deriving energy through the oxidation of nitrogen-containing compounds are commonly called nitrifying bacteria. Biological oxidation occurs in a variety of ways with different reactants and products. Organisms capable of oxidizing ammonia to nitrite are termed nitrosifiers, but are often referred to as nitrifiers. However, true nitrifiers are organisms that convert nitrite to nitrate. In cooling water systems, *Nitrosomonas* and *Nitrobacter* are the most common nitrifiers. Nitrogen fixing bacteria can convert molecular nitrogen to ammonia.

The nitrosifiers are most often found in open systems where ammonia contamination is possible. The oxidation of ammonia by bacteria produces nitrite. A pH drop caused by the conversion of ammonia to nitrite is often the clue to presence of nitrosifiers. If nitrifiers are also present, nitrate can be the final product.

Both nitrifiers and denitrifiers can exist in closed cooling water systems that are treated with nitrite-based corrosion inhibitors. Nitrifiers can deplete the nitrite-based inhibitor by converting nitrite to nitrate in oxygenated closed systems. This nitrification process produces nitric acid, so the action of nitrifiers in cooling water is generally associated with a drop in pH and an increase in nitrate levels. Corrosion can be caused by both the loss of nitrite and the production of acid.

Denitrifiers can be a common cause of denitrification in closed cooling systems. Denitrification is the process where microorganisms convert nitrate or nitrite to nitrogen gas. Denitrification is an anaerobic process and most relevant in tightly closed cooling water systems with nitrite treatment. The most common denitrifiers in cooling water systems are species of *Pseudomonas*, which are facultative anaerobes. These bacteria live in aerobic environments and use oxygen to grow but are adaptable to anaerobic conditions and use nitrite as a source of energy. If nitrite loss occurs in closed cooling water systems, denitrifiers or nitrifiers should be considered as a possible reason for the depletion.

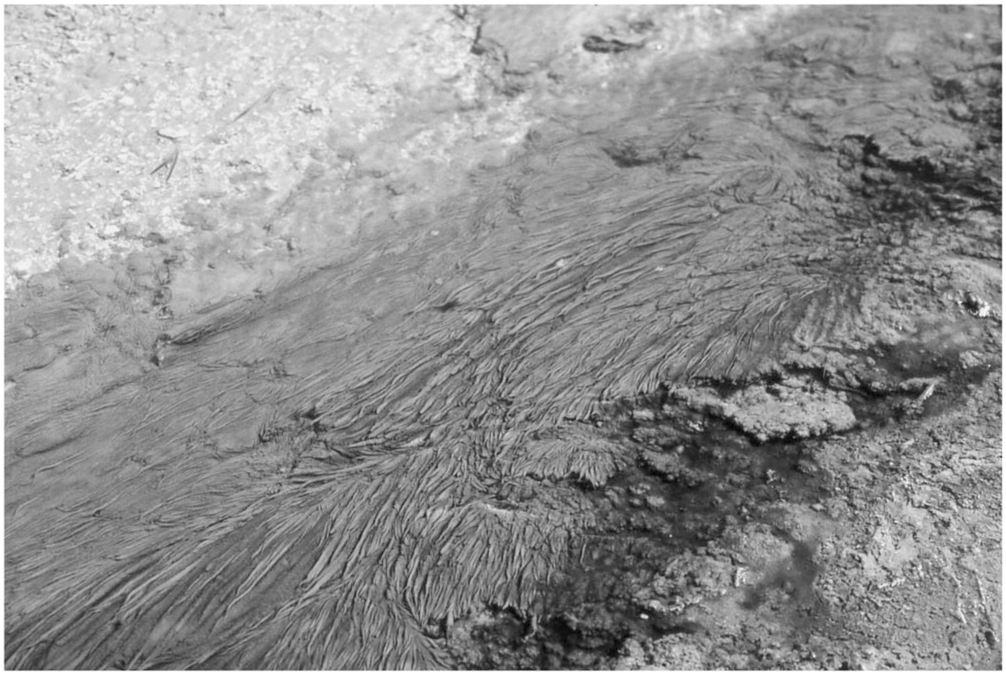


FIGURE 17.11 Thermophilic algae and bacteria growing in the outflow from one of the hot springs at Yellowstone National Park. (*NPS Photograph Courtesy of the National Park Service*.)

Clostridia and blue-green algae are examples of nitrogen fixing organisms. Dissolved molecular nitrogen in water can be converted to ammonia by either an aerobic or anaerobic process. The ammonia that is produced can promote the growth of other organisms in the water.

Algae

The thick, greenish layers of slime on a cooling tower deck or floating on a cooling pond are often algae. Algae need sunlight to grow, and therefore are found on open surfaces of a tower, ponds, and lakes. Algae contain chlorophyll and are capable of growing through photosynthesis, a process that uses sunlight to convert carbon dioxide and other nutrients into organic compounds for growth.

Two types of organisms can occur in these places—true algae and cyanobacteria. Algal cells are larger than cyanobacteria and contain chloroplasts, a defined structure within algae where chlorophyll is stored. The cyanobacteria are sometimes referred to as blue-green algae and have a different cell structure than true algae. Algae are plant-like organisms (Fig. 17.9), and blue-green algae are bacteria. Cyanobacteria also use chlorophyll and light to convert carbon dioxide and water to oxygen and complex organic molecules.

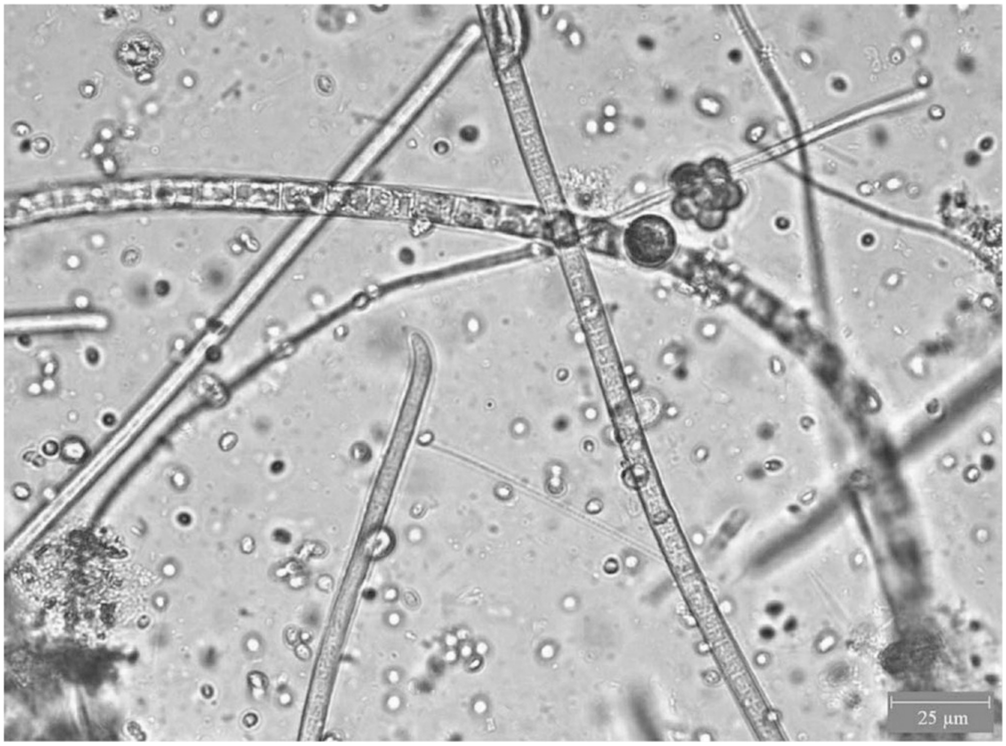


FIGURE 17.9 Photomicrograph of algal cells showing the complex cell clusters and long, plant-like strings of cells joined together (40×).

The primary problem caused by algae is the plugging of distribution decks on cooling towers, resulting in loss of efficiency of the cooling tower. Chunks of algae can break loose from the top deck and cause exchanger pluggage or fouling. The dense, fibrous mats of algae can also provide areas for subsequent growth of anaerobic bacteria under the algae deposits. Living or dead algae can also act as a food source for the slime-forming bacteria that can flourish in this environment.

Protozoa

Protozoa are single-cell organisms that have mobility and feed by ingesting particulate materials such as bacteria. There are four types of protozoa found in nature, with the amoeba being the most commonly observed in cooling water systems. Protozoa in cooling water systems are an indicator of serious microbial contamination. Protozoa often exist in an environment that contains a large and diverse bacterial population along with organic nutrients, on which the protozoa can feed. When protozoa are present, the bacterial population is generally out of control. Additionally, the presence of protozoa is of concern for *Legionella* control, since *Legionella* are known to use protozoa as hosts in order to survive (Chap. 20).

Fungi

Yeasts and molds are common fungi sometimes found in cooling water systems. Yeasts and molds grow in water-wetted areas, rather than on submerged surfaces. Growths of these organisms produce hard, rubbery slime on surfaces. Fungi grow on wooden structures, such as cooling tower fill and supporting members, and sometimes under bacterial or algal masses. Fungi generally attack the cellulose that provides the structural strength of wood. Fungal attack has different characteristics than chemical attack. Chemical attack most often causes delignification, whereas fungal attack can cause delignification, loss of cellulose, or both. Lignin is the binding material between the cellulose fibers in wood. Degradation of wood by chemical causes is covered in Chap. 16 (Cooling System Corrosion). The result of either fungal or chemical attack of wood is usually permanent loss of strength of the wood structure. The major characteristics of cooling tower lumber deterioration are shown in Fig. 17.10.

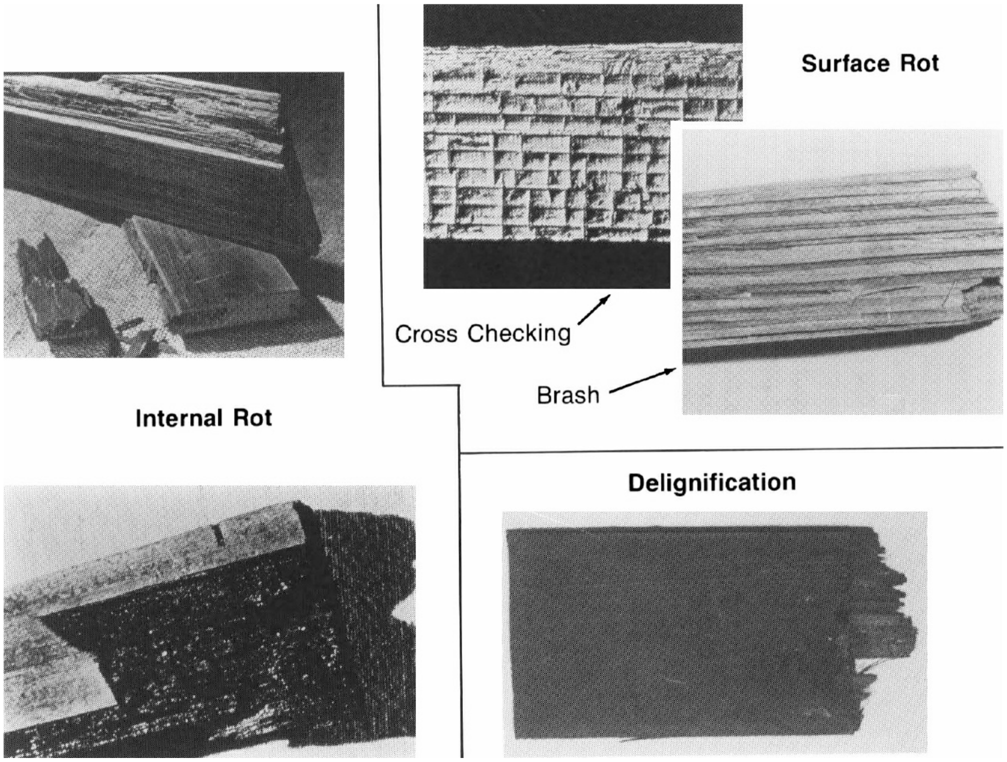


FIGURE 17.10 Typical examples of chemical or biological wood deterioration.

Fungi can cause either surface rot or deep, internal rot of wood. Organisms responsible for surface rot include members of the Ascomycetes class and Fungi Imperfecti. Ascomycetes are the fungi also responsible for the Dutch elm disease that devastated the elm tree population in the United States, Canada, and Europe. In cooling water systems, surface attack or soft rot occurs only in water washed or flooded portions of the cooling tower.

Fungi that produce deep or internal rot are members of the class Basiodiomycetes. These organisms consume wood components, such as cellulose and lignin, and are associated with brown rot, white rot, white pocket rot, and cubicle rot. In the Basiodiomycetes class, species of the genus *Lenzites* and *Poria* are commonly identified in samples of deteriorated wood.

The active growth of the wood-destroying fungi is confined to the surface layers and remains superficial, unless the wood is allowed to dry out frequently.

Factors Affecting Microbial Growth

An important factor affecting microbial growth is the degree of microbial contamination being introduced into a system. Another important factor is the amount of degradable material, or food sources, that are introduced to the tower. Microbes and their food can come from a variety of sources:

- Makeup water
- Airborne contamination
- Process leaks
- Organic debris
- Animal wastes
- Inadequate clean-up
- Inadequate dose of biocides (especially nonoxidizing biocides).

Controlling the source of microbial or organic contamination may not be possible depending on the source. For example, windblown dust that carries bacteria into a tower can be difficult to prevent. Controlling other factors of growth, such as the essential elements for growth or conditions suitable for growth, may also be difficult.

Suitable Conditions

Oxygen

Aerobic bacteria require oxygen and are found in aerated waters such as in a cooling water system. The main source of energy for aerobic bacteria is the oxidation of organic substances, with molecular oxygen as the electron acceptor. Anaerobic bacteria do not use oxygen and obtain energy from reactions of other substances or ions in solution. The reduction of sulfate to the sulfide ion and oxidation of ferrous ion to ferric ion are examples. Since anaerobes do not need molecular oxygen, anaerobic bacteria are found in oxygen-deficient areas, such as under deposits, in crevices, and in sludge.

Solution pH

Microbes have been found to exist in the broad pH range of 1 to 13. However, the most common microbes associated with water, algae and bacteria, prefer a neutral aquatic environment. Generally, yeasts and molds favor lower pH, in the range of 3 to 4. Bacteria and fungi can both contribute to industrial problems over a pH range of 3 to 10.

Temperature

Many species of microbes living in soil and water thrive in a rather broad temperature range of 50 to 125°F (10–52°C). Nature has produced a few organisms that can live at temperatures as low as 32°F (0°C) and as high as 212°F (100°C) (Fig. 17.11). Higher temperatures generally kill all common microbes, but scientists report finding life in hot springs and adjacent to ocean vents on the sea floor at temperatures of over 390°F (200°C). Therefore, most cooling water systems are within the ideal temperature range for microbial growth.

Sunlight

Organisms containing chlorophyll are able to use the radiant energy of the sun or artificial lighting to convert CO_2 to carbohydrates, which is needed for cell synthesis. However, not all radiant energy is useful to the cell and certain frequencies of radiation are harmful. Ultraviolet radiation is an example of one method of microbe control.

Biofilms

Biofilms are encountered in a variety of everyday environments. Plaque on teeth and slime found in a household drain are both examples of biofilms. Biofilms are the result of bacteria and other microbes that adhere to surfaces and produce a mixed population. Some bacteria produce an extracellular, glue-like substance (polysaccharide) to which a variety of particles can adhere.

In cooling water systems, microbes exist both in the flowing water (planktonic organisms) and attached to surfaces (sessile organisms) (Fig. 17.12). The vast majority of the microbes in a cooling water system are sessile and live in biofilms. The biofilms may contain particulate organic matter, mineral scale, corrosion products, sediment, and other microorganisms (protozoa, fungi, and algae). The contaminant sources can be the surrounding air, the source water, or process leaks.

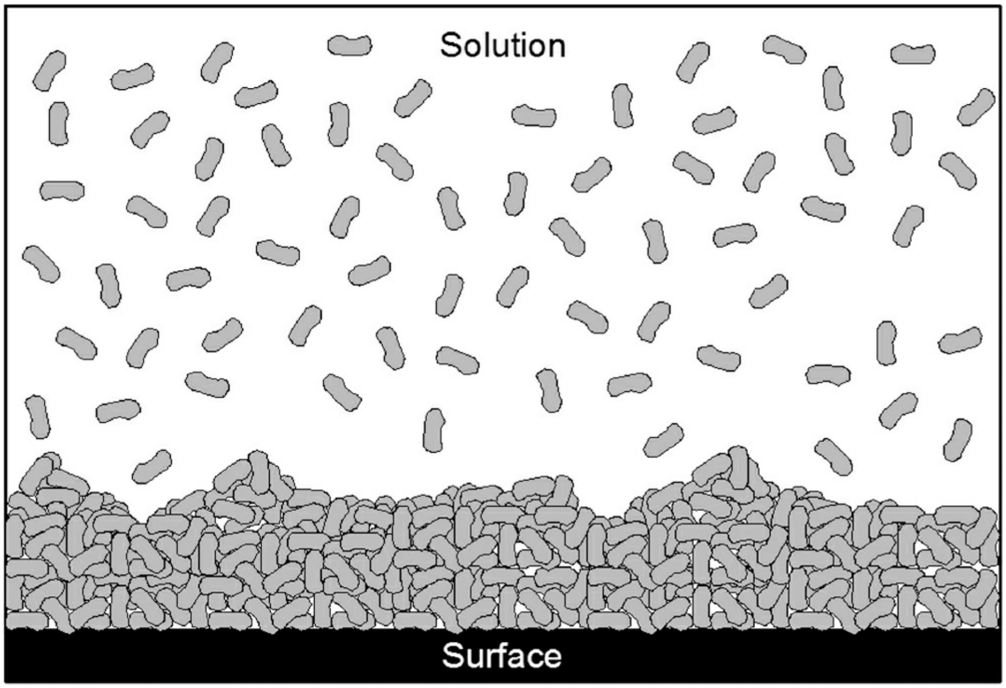


FIGURE 17.12 Biofilm on a surface may have 10 to 100 times as many sessile bacteria compared to the amount of planktonic bacteria floating in the water.

Formation and Growth

In cooling water systems, planktonic bacterial cells are routinely monitored. This method has proven to be a useful assessment of the microbial levels, despite the fact that a small minority of microorganisms in a cooling water system is planktonic. The sessile cells are the more prevalent microorganisms that are attached to the surfaces in the form of biofilms. Figure 17.13 shows a schematic representation of the stages of biofilm formation. Initially, planktonic cells are attracted to the surface, and weak bonds form between the bacterium and the surface. This may simply be an electrostatic attraction, which will depend on the type of microorganism, the type of surface, and a variety of conditions, such as pH and temperature. Once bonded to the surface, the microorganism changes. One visible change is that the sessile cells begin to secrete protein and polysaccharide slime. Cells turn on the gene responsible for synthesis of this slime after the cell is attached to the surface.

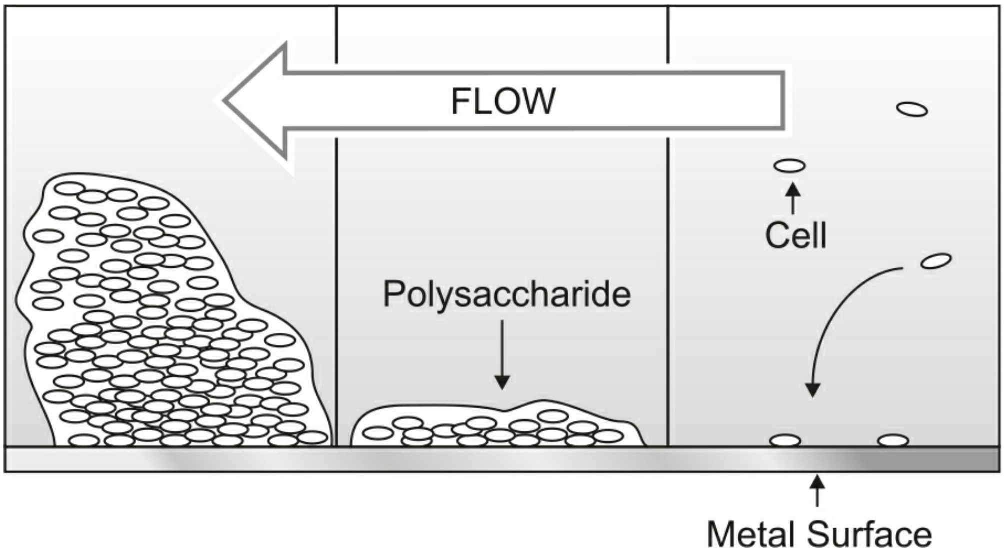


FIGURE 17.13 Stages of biofilm formation.

The bacteria in biofilms are able to grow, multiply, and attract other bacterial species as a complex community develops. Biofilms are dynamic in nature, with biomass sloughing off and being replaced by growth and attraction of other planktonic microorganisms. The rate of growth of a biofilm can be extremely fast, completely covering a surface in a matter of days.

Biofilm Advantages to the Microbes

Growth in biofilm provides several advantages to microbes. The biofilm provides a diverse consortium of organisms, increased availability of nutrients, and protection from antimicrobial agents. In a mixed, diverse population of microorganisms, exchange of metabolites can occur so the microorganisms can work together, each for their own benefit. The nature of the biofilm, especially the extracellular polymeric material, is believed to have the ability to attract and hold nutrients and ions that the bacteria in the biofilm need for growth.

Sessile cells are better protected from the environment than are free planktonic cells. Sessile bacteria are much more difficult to control with biocides than are planktonic bacteria. There are a few possible explanations for this phenomenon. The biofilm may prevent penetration of antimicrobial agents into the depths of the film. The concentration of antimicrobials in fluid beneath the biofilm surface would then be reduced. A likely reason for restricted penetration is that antimicrobials react with outer layers of the biofilm so the biocide is consumed before the biocide can penetrate into the film. Penetration rates are slower than the rate of reaction with the surface of the biofilm.

A further explanation is that a resistant microorganism may develop inside the biofilm. If nutrients are scarce, some microorganisms “shut down” or enter a waiting state, while other microbes may form spores. These would be resistant to kill by antimicrobials. Even in nutrient rich environments, attached microorganisms may have the ability to form resistant cells. All of these explanations for biofilm resistance to antimicrobial agents are the subject of ongoing research.

Problems Associated with Biofilms

Biofilms are responsible for reduced heat transfer efficiency in heat exchangers, reduced cooling tower efficiency, reduced flow, and increased under-deposit corrosion in cooling water systems. Biofilm can reduce heat transfer efficiency to a greater extent than other foulants on tube surfaces. Biofilms are at least four to five times more insulating than mineral scale deposit of comparable thickness (Refer to Fig. 17.2, shown earlier). In cooling towers, pluggage of the distribution deck can reduce flow and evaporation in the tower. Biofilm can contain corrosion products, mineral scale, and sediment in addition to microorganisms. Biofilms growing on parts of the tower can slough off surfaces and plug heat exchanger tubes (Fig. 17.14).

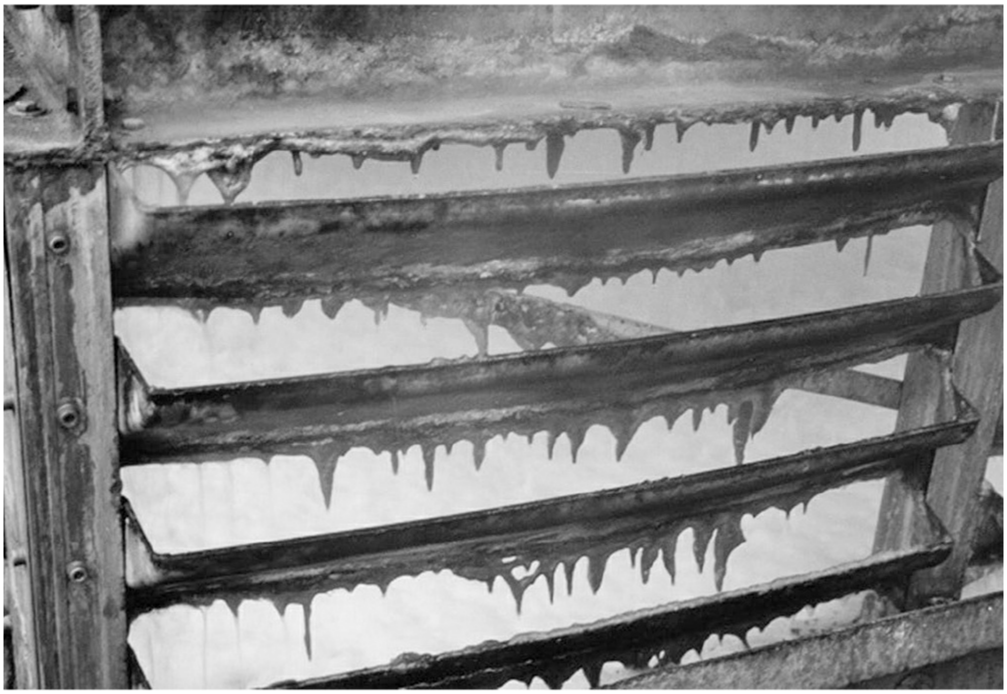


FIGURE 17.14 Example of biofilm hanging on water-wetted louvers near the basin of a cooling tower. The biofilm may contain bacteria, fungi, and inorganic material. If the biofilm falls off the louvers, plugging of heat exchanger tubes can occur.

The ability of biofilms to reduce flow in pipes is well documented. Fluid flowing through a pipe experiences drag from interaction with the pipe surface. This drag reduces the flow velocity and requires an increase in pressure to maintain a given flow rate. Biofilms have been shown to reduce flow by over 50% in large diameter piping. Most of the losses have been associated with increase in surface roughness creating greater fluid frictional factors. In some contaminated systems, biofilms can be formed as floc particles that move with fluid flow and can be considered as “fluidized” biofilms.

Corrosion due to biofilms can be as serious as the lost heat transfer efficiency. Microbial biofilms can cause concentration cell corrosion that occurs under deposits. Biofilms are responsible for microbiologically influenced corrosion (MIC). MIC is corrosion either directly induced or indirectly influenced by microbes and biofilms. SRB can affect corrosion by the metabolic production of sulfide ions (S^{-2}). Acid producing bacteria have already been mentioned as a source of corrosion in cooling water systems. These microorganisms and the acids they produce are responsible for the low pH microenvironments that can be observed under biofilms. Additionally, depletion of oxygen in the layers of biofilm in contact with the metal surface can lead to anaerobic conditions, setting up a condition referred to as a differential oxygen cell. All of these conditions create an environment where corrosion is enhanced. Under-deposit corrosion, concentration cell corrosion, differential oxygen cell corrosion, and MIC are all discussed more fully in Chap. 16 (Cooling System Corrosion).

Determining the Bacterial Population of Cooling Water

The differential microbial analysis (DMA) is a set of laboratory tests, which offers a profile of many microorganisms found in cooling water systems. DMA testing is not performed as frequently as on-site testing (like dip-slides described in Chap. 18) but periodic DMA testing can be an important part of an effectively managed microbial control program. It should be done periodically, with the frequency dependent on the level of microbial problems.

DMA provides important information about the microbiology of the cooling system. It can differentiate the bacteria in Table 17.1 (earlier in this chapter) by growing them on agar plates. Figure 17.15 shows a typical agar plate with mucoid and pigmented bacterial colonies grown from a cooling water sample. Other organisms, like algae, protozoa, and fungi can be determined by microscopic observation. Figure 17.16 shows an example of a DMA report with a typical distribution of organisms found in an open recirculating cooling water system. In this water sample, a variety of typical aerobic bacteria are present, a very small amount of anaerobic bacteria may be present, yeasts and molds are very low, and no other troublesome organisms are found.

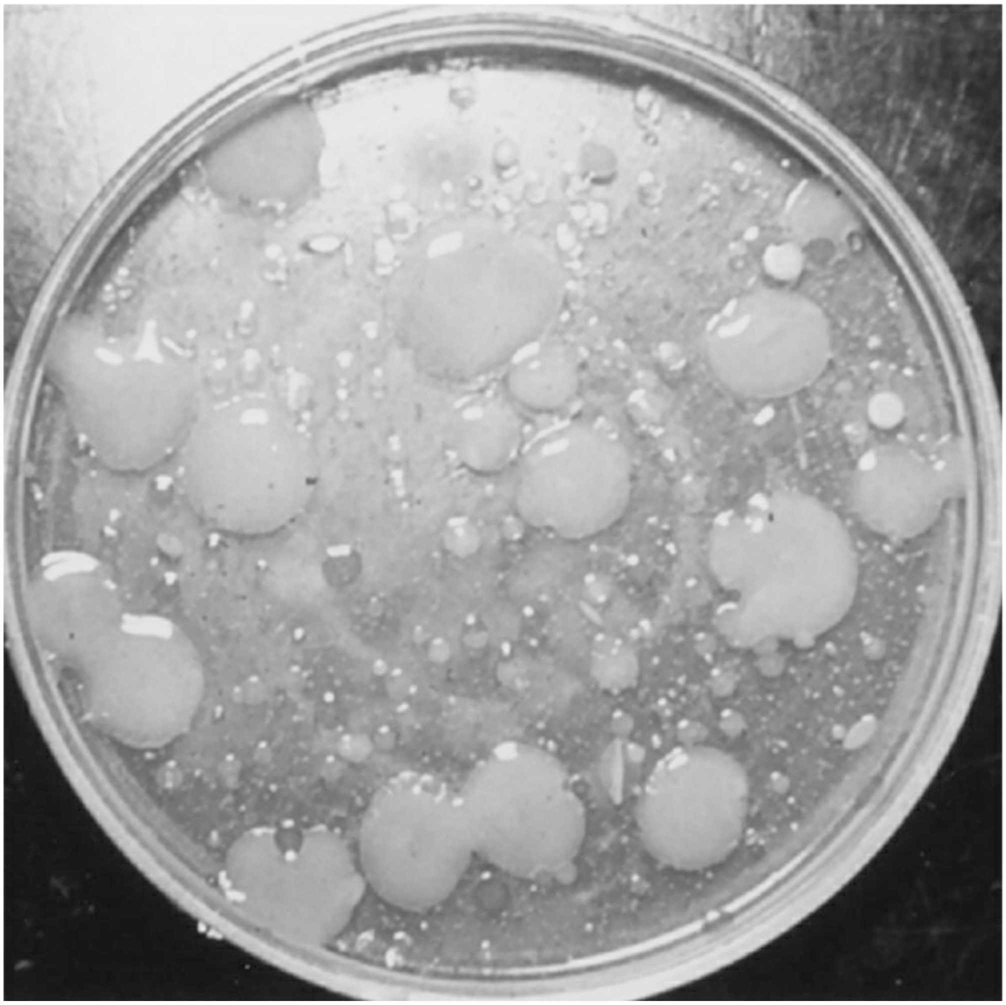
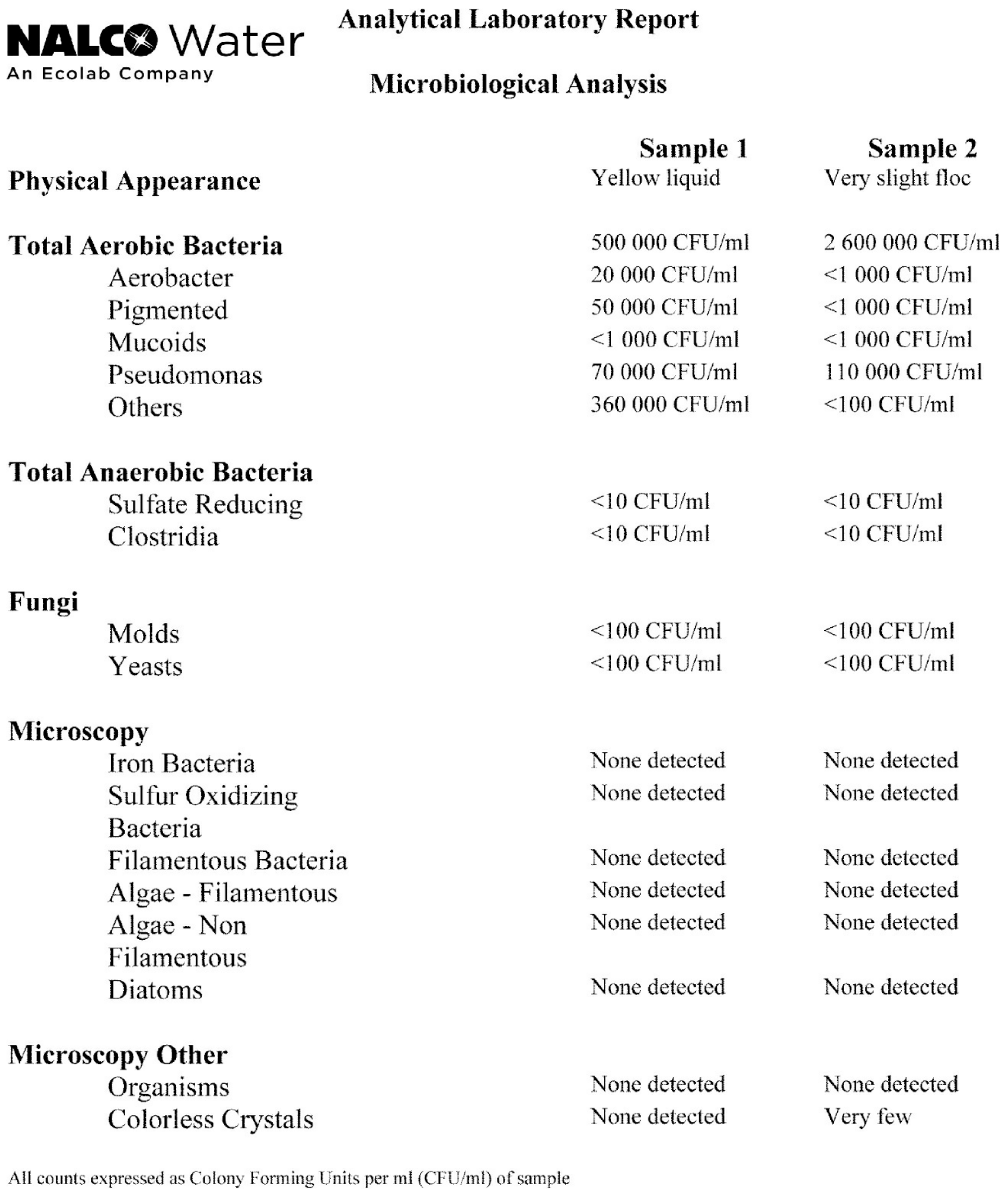


FIGURE 17.15 Example of bacterial cell cultures from cooling water system grown on an agar plate as part of a DMA.



NALCO Water
An Ecolab Company

Analytical Laboratory Report

Microbiological Analysis

	Sample 1	Sample 2
Physical Appearance	Yellow liquid	Very slight floc
Total Aerobic Bacteria	500 000 CFU/ml	2 600 000 CFU/ml
Aerobacter	20 000 CFU/ml	<1 000 CFU/ml
Pigmented	50 000 CFU/ml	<1 000 CFU/ml
Mucoids	<1 000 CFU/ml	<1 000 CFU/ml
Pseudomonas	70 000 CFU/ml	110 000 CFU/ml
Others	360 000 CFU/ml	<100 CFU/ml
Total Anaerobic Bacteria		
Sulfate Reducing	<10 CFU/ml	<10 CFU/ml
Clostridia	<10 CFU/ml	<10 CFU/ml
Fungi		
Molds	<100 CFU/ml	<100 CFU/ml
Yeasts	<100 CFU/ml	<100 CFU/ml
Microscopy		
Iron Bacteria	None detected	None detected
Sulfur Oxidizing Bacteria	None detected	None detected
Filamentous Bacteria	None detected	None detected
Algae - Filamentous	None detected	None detected
Algae - Non Filamentous	None detected	None detected
Diatoms	None detected	None detected
Microscopy Other		
Organisms	None detected	None detected
Colorless Crystals	None detected	Very few

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

FIGURE 17.16 Typical DMA report from an open recirculating cooling water system under reasonably good control.

The DMA monitors planktonic bacteria, those floating in the water, or sessile bacteria, which are those on surfaces. Planktonic bacteria are measured in water samples while sessile bacteria are measured in samples swabbed from a surface in the cooling water system. It is the sessile bacteria on the exchanger surfaces that affect the heat transfer efficiency of the system and can cause under-deposit corrosion. A very high proportion of the bacteria in cooling systems live on system surfaces. Monitoring the planktonic bacteria can give an indication of the bacterial population of a system, but there is no correlation between planktonic counts and the amount of sessile bacteria on surfaces of a system. Therefore, control of microbial growth is essential for optimum results in cooling systems.

[1] Zelver N., Characklis W., Roe F., Annual Meeting of the Cooling Tower Institute Paper TP239A, CTI (Cooling Tower Institute), Houston, U.S., 1981.

CHAPTER 18

Cooling Water Monitoring

Monitoring of cooling systems is critical to ensure optimum performance and to maximize efficiency. Generally, monitoring can be divided into methods to evaluate performance and system control. Performance evaluation includes methods to determine the amount of deposition, corrosion rates, and microbial growth and fouling. Methods to evaluate system control generally involve analysis of water samples.

Deposition Monitoring

Many different deposit monitors are used in cooling systems, ranging from a simple mesh screen to entrap deposits to small shell-and-tube heat exchangers that must be opened to observe deposition. The most common types involve a heated tube to simulate a heat exchange surface. Specialized biofouling monitors range from boxes containing removable test surfaces that entrap microbial organisms to pressure drop monitors that measure change in pressure across a smooth tube as microbial fouling occurs. Online deposit monitors, based on a piezoelectric crystal, have been developed that measure the rate of deposition on the crystal surface.

Removable sections of tower fill and strain gauges are often used to monitor fill fouling in cooling towers. New nonintrusive technology to map tower fill density and location is also used.

Heated Tube Deposit Monitors

These monitors have an internally heated tube, so that the surface exposed to water can be observed as deposition occurs. The more accurately the monitor simulates conditions of the heat exchanger in question, the more closely deposition simulates results in the exchanger. Even so, the deposit monitor is only a simulation of conditions in an exchanger. Thus, results must be interpreted with care and correlated to actual exchanger performance and inspections.

Tube-based deposit monitors are available in a variety of styles. A typical deposit monitor allows for continuous on-site monitoring of deposition on a heat transfer surface in a cooling water system. Metallurgy of the sample tube, water flow rate, heat flux, and skin temperature can be selected to simulate conditions of a specific heat exchanger. Tube skin temperature can be monitored to allow calculation of heat transfer coefficient (U value) or fouling factor of the deposit monitor tube. Trends of fouling rate can be obtained to relate to program performance in the plant. Another commercially available unit is the Deposit Accumulation Testing System (DATS® made by Bridger Scientific, Inc.) as shown in Fig. 18.1. There are several different configurations of this unit. The DATS monitor operates in a similar manner to the tube-based monitor.

FIGURE 18.1 Example DATS® deposit monitor. (*Courtesy of Bridger Scientific*.)

Pressure Drop Microbial Fouling Monitors

An example of this type of deposit monitor is shown in Fig. 18.2. Typically, a specially designed tube with a differential pressure gauge is used to measure pressure drop across the tube. As biofilm develops, pressure drop increases; as biocontrol is regained, pressure drop correspondingly decreases. Biofilms as thin as 1 mil (25 μm) can usually be detected.

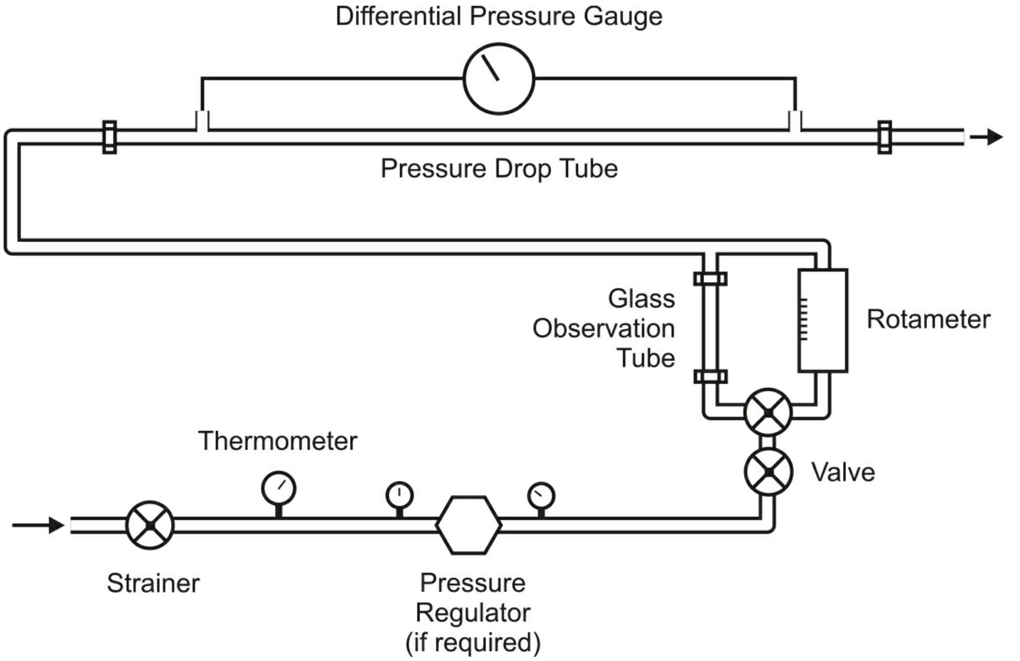


FIGURE 18.2 Typical biofouling monitor using a pressure drop tube.

Real-Time Deposit Monitoring

A piezoelectric quartz crystal microbalance can monitor changes in fouling over short time periods and is sometimes called a real-time monitoring device (Fig. 18.3). The crystal vibrates when current is applied, and vibration frequency changes in proportion to the mass of deposition on the crystal surface. Changes in deposition can be measured rapidly, and by monitoring changes in the signal over time, trends of fouling from both mineral scale and soft deposits like microbial slime can be obtained. The crystal surface may not be heated, and the surface may have different characteristics from a heat transfer surface. These monitors are generally used for shorter periods than tube-style deposit monitors. They are most useful for showing the effect of changing conditions or programs rather than simulating an actual exchanger fouling rate.

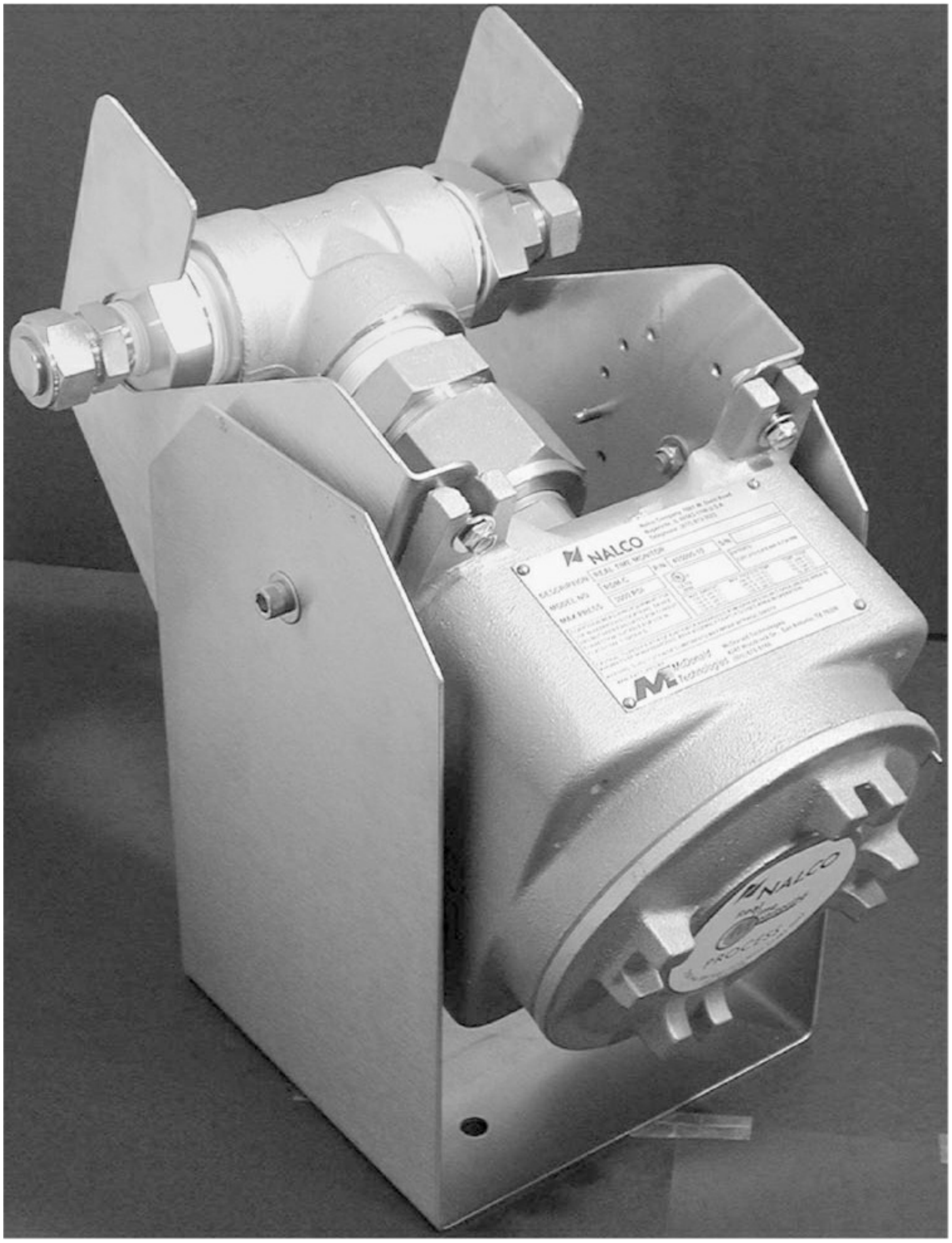


FIGURE 18.3 Example of a real-time deposit monitor.

Corrosion Monitoring

The purpose of corrosion monitoring is to assess or predict corrosion behavior of a system. Corrosion monitoring is standard practice in the water treatment industry and has several uses:

- To make a rough prediction of equipment life
- As a diagnostic tool to help solve corrosion problems
- Show effectiveness of treatment programs or effect of changes to operating parameters
- Correlate corrosion trends to control parameters

The particular corrosion monitoring technique selected depends upon its applicability to the system and information desired. Most corrosion monitoring techniques are best suited to situations where corrosion is of a general nature, but some techniques provide information on localized attack such as pitting. Specific examples are given in Table 18.1, with description of what is measured and application of each monitoring technique. More than one method may be necessary to properly evaluate efficacy of a treatment program in a system. Each technique has specific characteristics that lend themselves to different applications.

Method	Measures	Applications
Corrosion coupons (small, metal specimens)	Average corrosion rate is determined by mass change of coupon over a period of typically 30–90 days. Can be used for pit depth measurements.	Best for uniform corrosion under steady-state conditions. Can show localized attack by pitting and under-deposit corrosion. Coupons are available for most alloys.
Linear polarization resistance (LPR) (e.g., Nalco NCM100 and Corrater)	Instantaneous corrosion rate is measured by electrochemical polarization between two electrodes. Tendency for pitting (pitting index) can be measured.	Water must have sufficient conductivity to provide suitable measurement of corrosion rate. Suitable for common engineering alloys.
Electrical resistance (ER) (e.g., Corrosometer)	Corrosion rate is determined by electrical resistance change from thickness loss of a corroding metal wire. Uniform corrosion rate is assumed in calculation.	Works in zero to high conductivity environments, either liquid or vapor using most alloys. Gives general corrosion rate even if localized corrosion is occurring.
Analytical monitoring	Concentration of dissolved or suspended species in water, such as corrosion products, pH, and conductivity. Does not measure corrosion rate directly.	Trends of dissolved or suspended corrosion products may be proportional to changes in corrosion rate. Precipitation of these corrosion products limits technique effectiveness.
Deposit monitors [e.g., Deposit Accumulation Testing System (DATS)]	Visual observation of corrosion on heat transfer surface. Metal tube can give average corrosion rate from mass loss data and pit depth measurements.	Suitable in simulating conditions of heat exchanger, if alloy is the same as in the exchanger and water temperature and heat flux are similar. Heat transfer tubes can be made from most alloys.

Corrater® and Corrosometer® are Trademarks of Rohrback Cosasco Systems; DATS® is a Trademark of Bridger Scientific, Inc.

TABLE 18.1 Examples of Monitoring Techniques with Parameters Measured and Applications

Corrosion Coupons

The simplest corrosion monitoring technique is to place a metal coupon (small strip of metal) in flowing cooling water for a given time. Coupons are made from many alloys, and appropriate alloys should be selected to match metals in the system.

Coupons must be placed in a coupon test rack for best comparison to system results, and for best consistency from one exposure period to another. Data gathered have value only if coupons are properly installed. A typical installation of coupon and holder for cooling systems is shown in Figs. 18.4 to 18.6. Coupons should be placed where conditions simulate the environment being evaluated. For example, if the objective is to evaluate corrosion potential in a critical exchanger, a coupon rack should be installed at the outlet of this exchanger, so that water temperature is representative of that exchanger. Deposit monitor tubes are also used to approximate heat exchanger corrosion rates, since tubes are heated to similar skin temperatures.

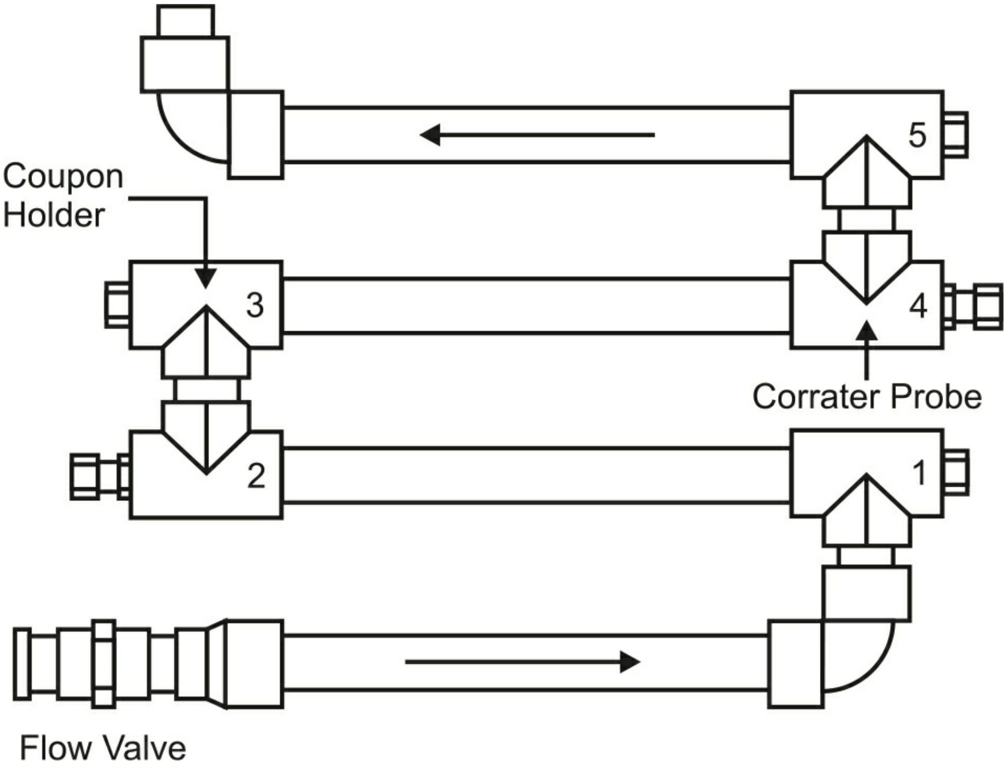


FIGURE 18.4 Illustration of a corrosion test rack.

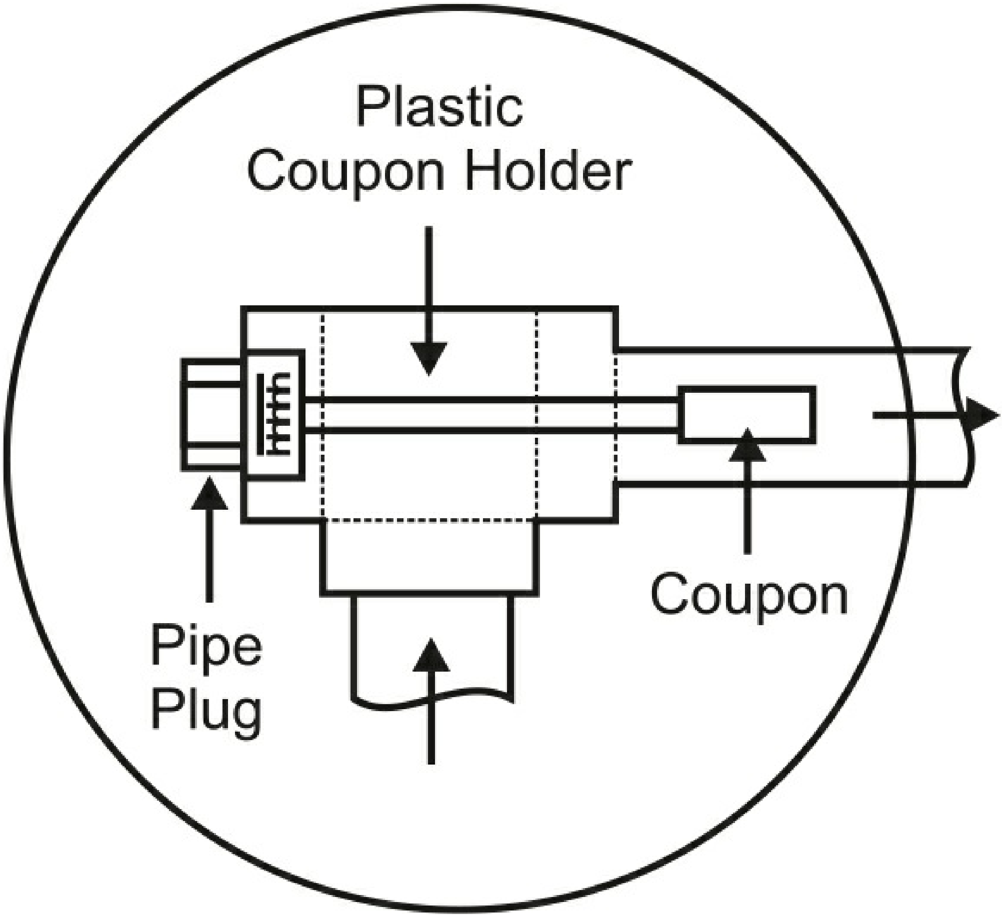


FIGURE 18.5 Illustration of a correct corrosion coupon installation in the rack.

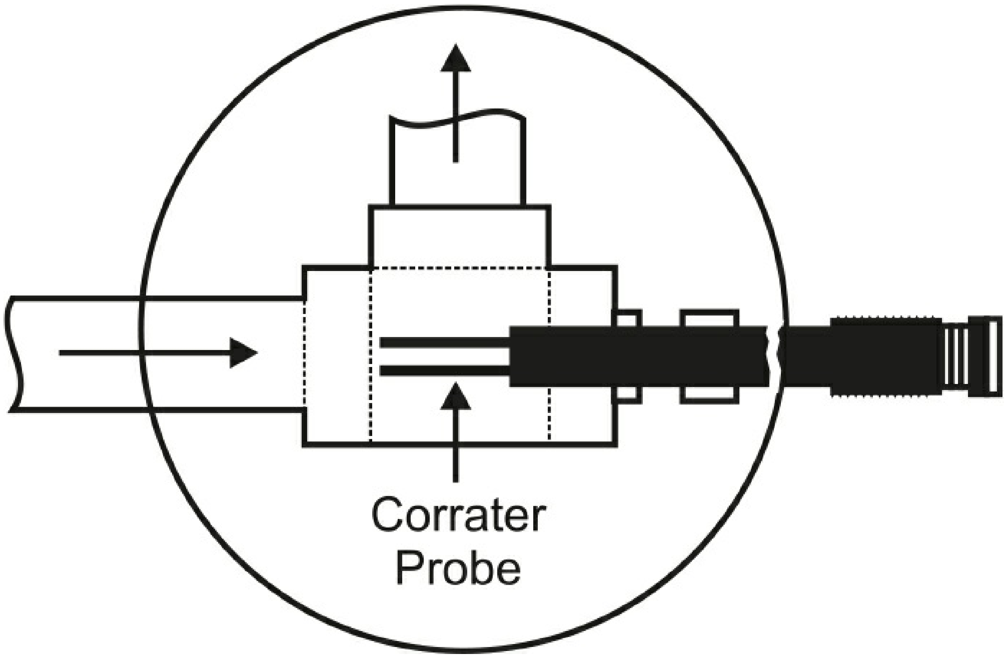


FIGURE 18.6 Illustration of a correct LPR probe installation in the rack.

Coupon Exposure

Typically, coupons are exposed to system water for 30 to 90 (90 preferred) days. This exposure period is needed, particularly for mild steel, to avoid abnormally high corrosion results from initial corrosion effects during the first few days of installation. Initial corrosion rates on steel coupons can be very high, because the bare metal surface is in an active state due to lack of a protective oxide layer. Figure 18.7 shows decrease in corrosion rate with exposure time for mild steel. Steady state is normally achieved in several days to a week, depending on conditions. A common approach is to use three sets of coupons, placed in a test rack and changed in sequence of 30-, 60-, and 90-day intervals. Normally, with longer exposure period, coupons more closely approximate conditions in the system.

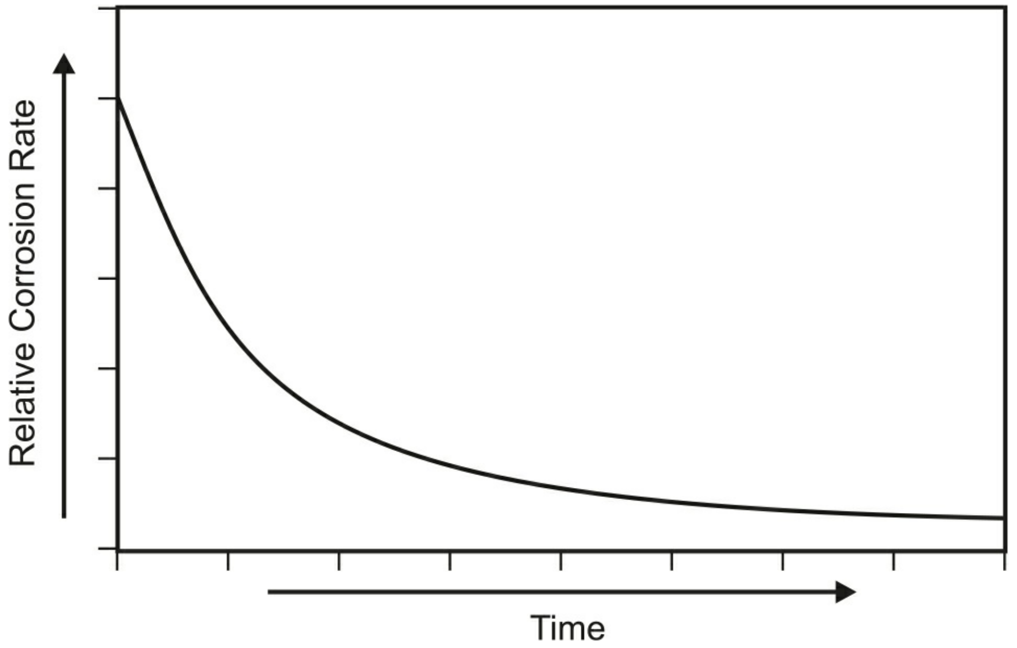


FIGURE 18.7 Coupon corrosion rate is very high when first installed in cooling water, decreasing to steady state after a few days to a week.

It is common to install several corrosion coupons of the same type, so that one can be removed for analysis each month (after the appropriate 90 days). In this way, monthly corrosion data can be reported.

Occasionally, such as during a program transition, it is desired to obtain data after as short as one month after transition. This can be done; however, there should be a one-month exposure coupon taken just prior to the conversion, as a comparison. As stated, exposure of that short a period will show abnormally high corrosion rates, compared to coupons exposed for 90 days. This way timely results can be seen, but also compared to the previous conditions. Typical 90-day results would then be used for final determination of transition success.

Coupon Evaluation

After coupons are removed from the system, they should be evaluated by a metallurgical analytical lab. This involves cleaning the coupon in a specialized manner, determining the new mass of the coupon, and calculating the corrosion rate based on mass loss. The corrosion rate is reported in mils per year (mpy) or micrometers per year (µm/y), along with a description of the type of corrosion attack. Common standards for description of the type of corrosion are:

- General corrosion—uniform corrosion over entire surface
- Localized attack—isolated areas of corrosion
- Pitting—small, deep, isolated areas of corrosion where depth of penetration exceeds width of pit mouth

Examples of these are shown in Fig. 18.8. When pitting or localized corrosion occur, the general corrosion rate can grossly underestimate severity of a corrosion problem. In this case, type and depth of attack should be noted.

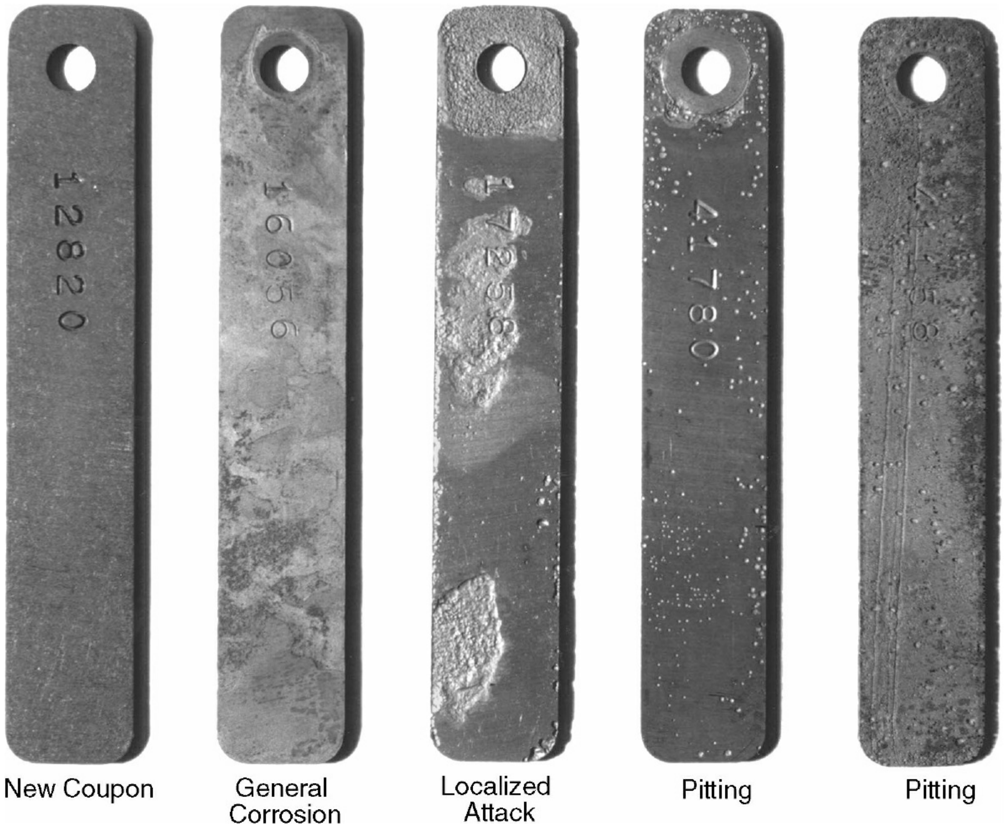


FIGURE 18.8 Examples of corrosion that fit standard descriptions of types of corrosion on a mild steel coupon.

Actual pit depth can be measured using a specially designed pit depth microscope, schematically shown in Fig. 18.9. This direct measurement determines actual penetration of metal during exposure of the coupon. Typical microscopes can measure pit depth to a resolution of 0.1 mil (2.5 μm). The coupon report of corrosion rate should include this pit depth measurement, in addition to an average corrosion rate.

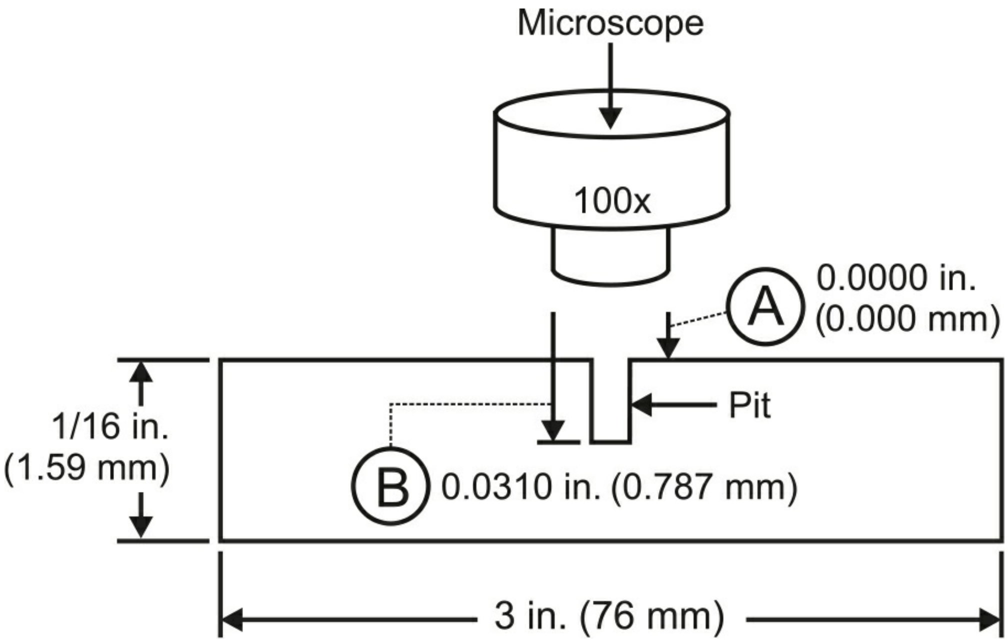


FIGURE 18.9 Measurement of pit depth by difference between coupon surface and bottom of pit.

Typical Range of Corrosion Rates

The desired goal for corrosion rates should be determined individually for each given system. Typical classifications for corrosion rate values are shown in Table 18.2. Note that these are typical definitions or descriptions of different ranges of corrosion coupon results. Individual system operators may have tighter requirements for corrosion performance, depending on criticality of the process involved.

Corrosion Rate, mpy (μm/y)		
Mild Steel Coupons	**Copper Alloys**	**Description of Results**
<1 (<25)	<0.1 (<2.5)	Excellent (negligible corrosion)
1–3 (25–76)	0.1–0.25 (2.5–6.4)	Very good (minimal corrosion)
3–5 (76–127)	0.25–0.35 (6.4–8.9)	Good (moderate corrosion)
5–8 (127–203)	0.35–0.5 (8.9–12.7)	Poor (moderately high corrosion)
8–10 (203–254)	0.5–1.0 (12.7–25)	Bad (high corrosion)
>10 (>254)	>1.0 (>25)	Unacceptable (severe corrosion)

TABLE 18.2 Generally Accepted Ranges for Corrosion Performance

Electrochemical Corrosion Monitoring

The two most common electrochemical techniques for online, real-time corrosion monitoring are linear polarization resistance (LPR) and electrical resistance (ER). Table 18.1, shown earlier, provides some characteristics of these two methods. Corrosion rate trend data generated by these methods are more valuable than any single reading taken alone. Changes in trend data can be very valuable for troubleshooting.

Linear Polarization Resistance

Corrosion occurs due to electrochemical corrosion reactions. The rate of corrosion is proportional to current flow in the electrochemical cell. Current flow is dependent on resistance of the solution (solution resistance) and resistance caused by any inhibitor film on the metal surface (polarization resistance). In typical conductivity of cooling water, solution resistance is negligible. Therefore, the corrosion rate can be determined with LPR based on polarization resistance alone. The LPR technique measures instantaneous corrosion rate, since a complete scan takes less than a minute.

LPR monitors can provide corrosion rate data within a few hours to several days after installation. Depending on metal used, probe tips need some time for passivation by treatment in the system. This instrument is well suited to applications where upsets or other accelerated corrosive conditions must be detected quickly, so that remedial action can be taken. The corrosion rate obtained with LPR techniques assumes uniform corrosion, but some instruments can show pitting tendency (pitting index).

LPR can be inaccurate in low conductivity waters such as once through cooling water, soft cooling water, and boiler condensate, because the magnitude of solution resistance can be significant. (Remember, LPR measures the sum of solution and polarization resistance as the corrosion rate.) Two commercially available devices that use LPR are the Corrater made by Rohrback Cosasco Systems and the Nalco NCM100. The NCM100 (Fig. 18.10) and some models of the Corrater have compensation for low conductivity solutions, and can be accurate in water with conductivity as low as 10 µS/cm.

FIGURE 18.10 Example of an LPR-based instantaneous corrosion monitor.

Electrical Resistance

Conventional electrical resistance (ER) probes for corrosion rate measurements consist of a metal wire element embedded in a water-resistant material. As corrosion proceeds, cross-sectional area of the metal wire decreases, causing an increase in ER of the wire. By measuring change in electrical resistance, the corrosion rate can be determined. This ER technique can be used for corrosion rate measurements in liquids or vapors. The liquid does not have to be conductive to obtain results. The disadvantage is that ER does not measure instantaneous corrosion rate. Usually, at least a week is required to obtain a significant change in electrical resistance, especially in well-treated cooling water systems. In addition, the ER method cannot detect localized corrosion such as pitting. The Corrosometer, manufactured by Rohrback Cosasco Systems, is an example of an ER corrosion monitor.

Corrosion Product Monitoring

Monitoring either iron concentration for steel components or copper concentration for copper-based alloys can be useful for evaluating corrosion trends. This method assumes that the concentration of ions in solution released by corrosion reactions is an indication of the severity of corrosion. This assumption is not always correct, because metal ion concentration in the sample can be affected by a variety of system conditions, such as:

- Iron in the makeup water directly influences iron concentration in the system.
- Iron deposits in the system or airborne contamination may release iron into water.
- Sample collection techniques can affect analytical results for sparingly soluble ions like iron.
- Accurate iron testing is required; the difference between 0.6 mg/L and 0.8 mg/L may be insignificant.
- Iron corrosion products tend to precipitate.

Even with these constraints, corrosion product ion analysis can still be valuable for monitoring trends in corrosion. To effectively use this technique, a procedure must be established and rigorously followed, so that analysis of results is of value. The procedure should include sampling protocol, sampling frequency, and using the same analytical method for all samples. Statistical process control (SPC) techniques should be used for analyzing variations in trends.

Biological Growth Monitoring

Monitoring biological growth and biofouling are essential for proper control and operation of cooling systems. A variety of techniques is available, including biofouling monitors described earlier in this chapter. Using several methods to monitor a system generally yields the best results.

Lab Methods

A common method to determine the quantity and type of organisms in a cooling system is to send a water sample to a special analytical laboratory for microbial analysis. Several methods including growing bacteria on agar plates, microscopic analysis, and wood analysis for fungi are available.

Plate Count Methods

The most common technique to estimate the number of living (viable) cells in a water sample is the plate count or colony count method. Small amounts of different dilutions of the water sample are applied to agar growth medium in Petri plates. After a suitable incubation time (usually two to three days), the number of colonies that have developed is estimated. The number of colony-forming units per milliliter (CFU/mL) is determined using the dilution factor for that plate. Many different growth media are available. One agar type is used to produce total aerobic colony count, while other types grow specific bacteria like slime forming, anaerobic-corrosive, or nitrifying bacteria.

This is the basis for the differential microbiological analysis (DMA) used in cooling water testing to gain an understanding of the types of microorganisms present. Total count is an indicator of relative contamination of a cooling system. Increase or decrease of total count by a factor of 10 or more signals significant change in the level of microbial contamination. However, total count understates the true bacterial population and does not measure bacteria in biofilm on surfaces. More detail on this method and an example DMA report is shown in Chap. 17.

Microscopic Examination

Two distinct types of microscopy are employed in examination of microbiological samples. The light microscope is used to see intact cells, while the electron microscope with its greater resolving power is used to study cell structure and details. The light microscope is valuable in classification of bacteria by various cell morphology, and the reaction of cells to various stains. Gram stain reagents are applied to microorganisms that have been fixed to a slide, and observation of the color of the cell is done with a microscope. Gram-positive bacteria appear purple, and gram-negative bacteria appear red. Figures 18.11 to 18.16 show a variety of different microbes that can be found in cooling systems.

FIGURE 18.11 A photomicrograph of a Nematode.

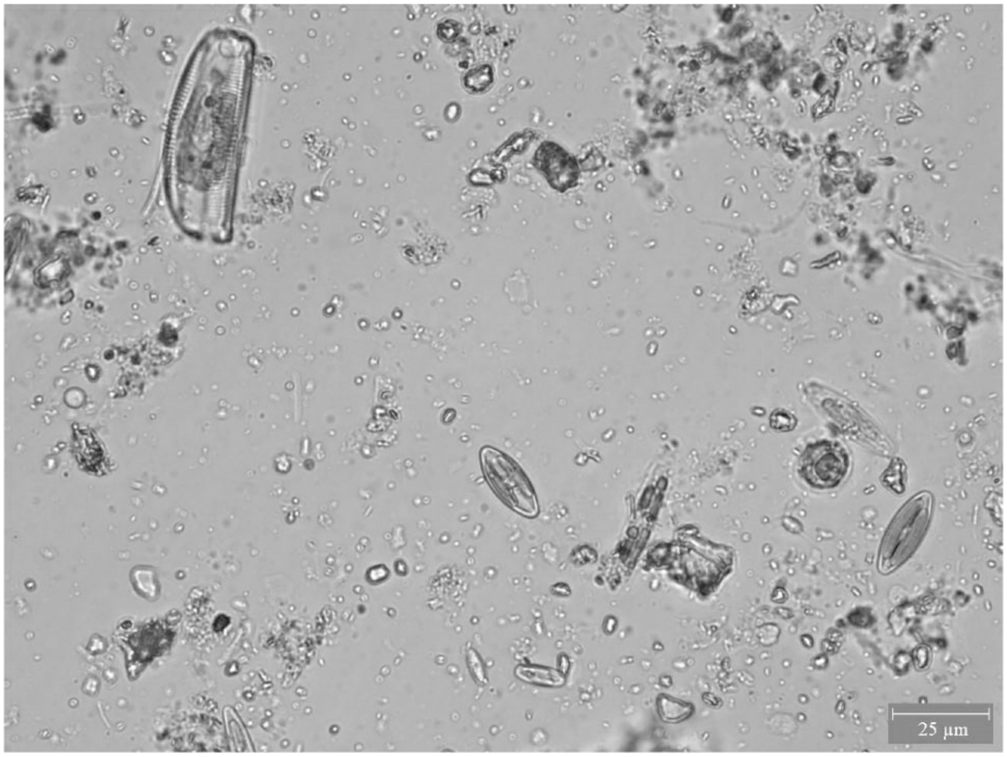


FIGURE 18.12 A photomicrograph of Diatoms.

FIGURE 18.13 A photomicrograph of Filamentous algae.

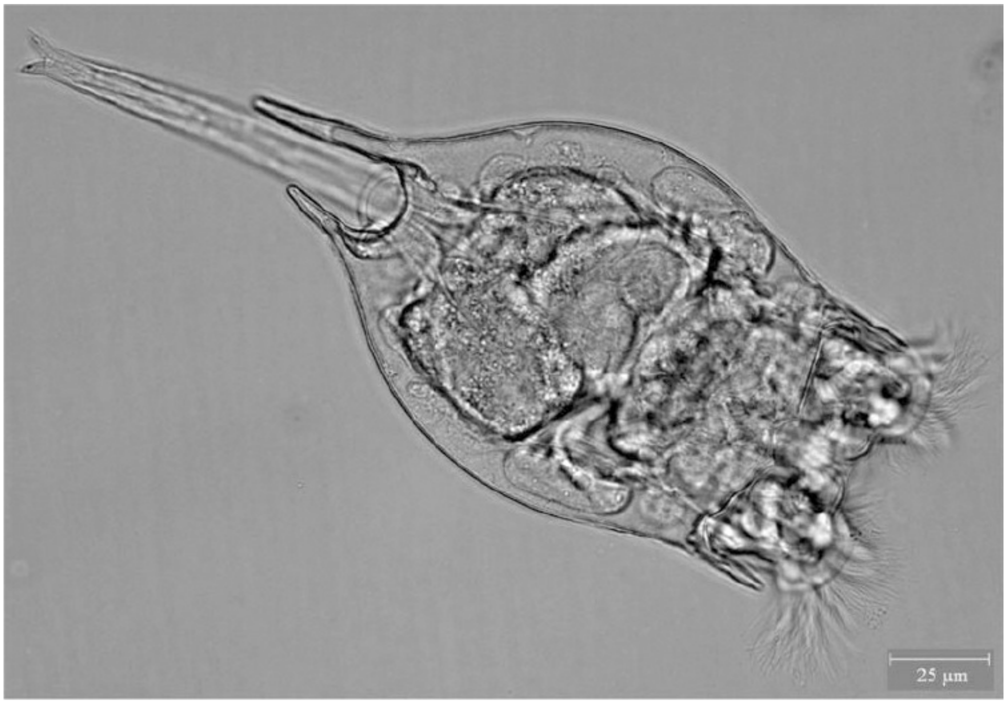


FIGURE 18.14 A photomicrograph of a Rotifer.

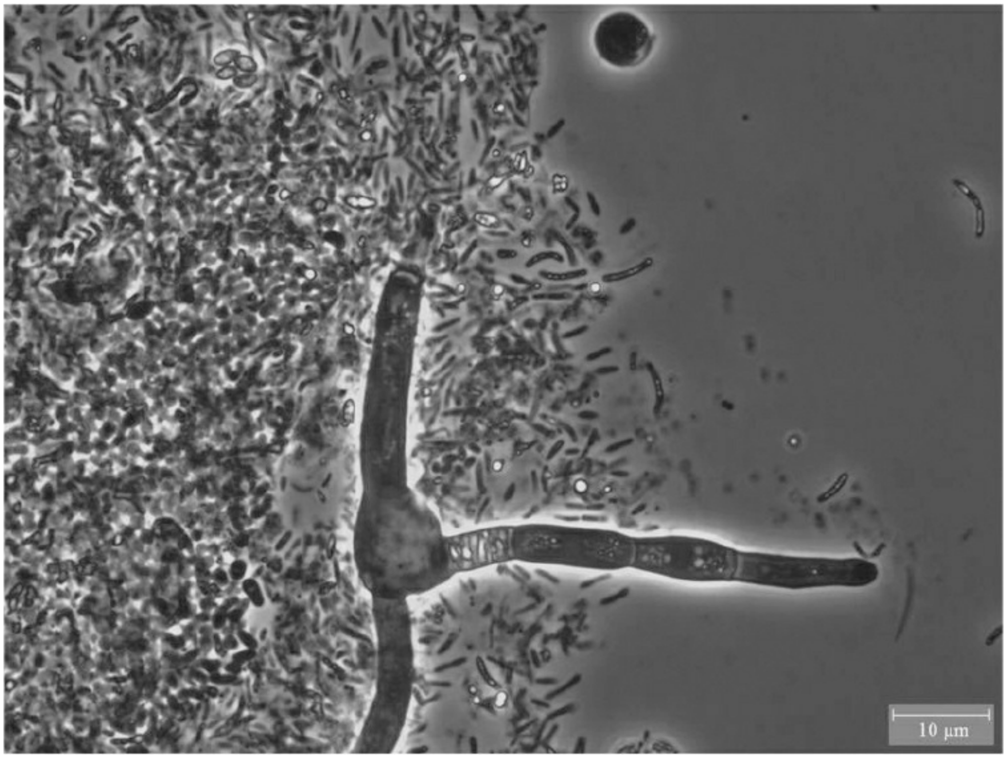


FIGURE 18.15 A photomicrograph of a fungal filament.

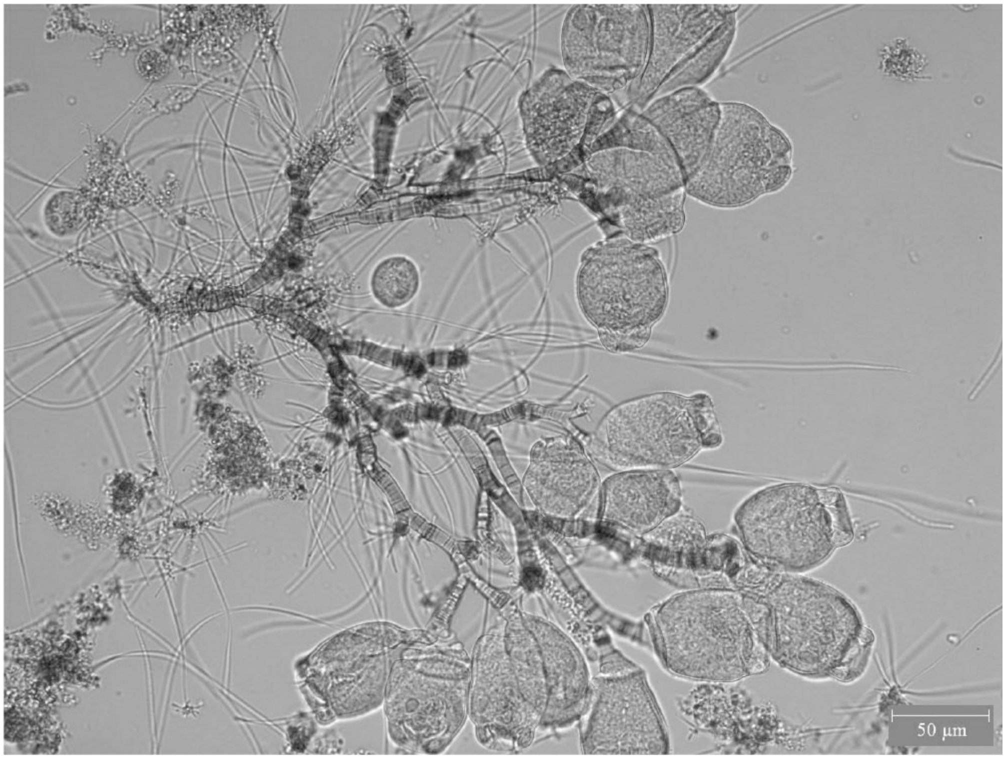


FIGURE 18.16 A photomicrograph of colonial stalked ciliates.

Wood Samples

Wood in a cooling tower can be monitored periodically to prevent long-term fungal deterioration. Monitoring is usually conducted with wooden test specimens placed in the cooling tower. Test samples can be submerged, placed in constantly wetted areas exposed to air (fill section), or placed in areas with only moisture contact (plenum area). After a period, samples are analyzed in a laboratory for presence of fungi and their resistance to fungi growth. Results indicate if tower lumber is infected and what actions are required to minimize wood deterioration.

Field Methods

On-site testing is needed to provide more rapid information compared to sending a sample for detailed lab testing. Several methods exist, including a variation of the lab plate count method.

Dip Slides

The dip slide is a widely-used field test to monitor microbial activity in a system. This test is a simple version of the plate count method. Growth medium (dip slide) is immersed briefly in the water sample, and the slide is incubated in its container. A biologically active dye is present so that stained colonies are easily observed (Fig. 18.17). The slide is compared to a set of standard slides (Fig. 18.18) to estimate CFU/mL in the sample. Common dip slides provide an estimate of total aerobic bacteria and fungi as part of the same test. Other growth media are available to test for sulfate-reducing bacteria (SRB).

FIGURE 18.17 Microbes are collected and cultured by pretreated elements, which are easily incubated in the sampling container. (*Courtesy Millipore Corporation*.)

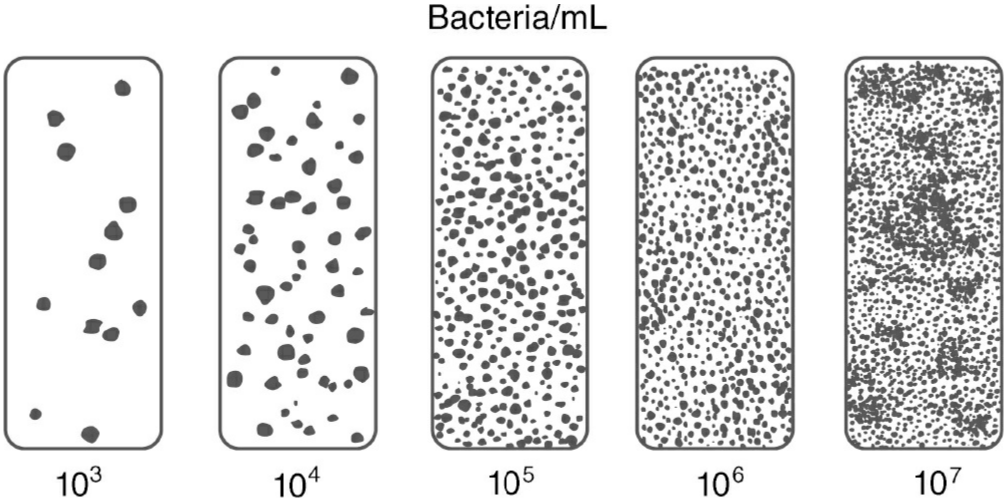


FIGURE 18.18 Chart for interpretation of dip slide results.

Dip slides are easy and quick to use, economical, and sensitive to a range of microbial levels. Results are available in two days, without need to send samples to a laboratory. However, they do not detect all types of microorganisms and cannot differentiate wide varieties of microorganisms.

Quick Dye Tests

Quick tests exist for rapid screening to estimate microbial growth in a water system. A water sample (usually 500 mL) is filtered through a fiberglass filter. Microorganisms collected on the filter pad are visualized with an indicator dye, which reacts with living microorganisms. Intensity of the color is indicative of the number of colony-forming units present. The method is a rapid and inexpensive means to determine if high bacteria levels are present. The main disadvantage is that 10^5 CFU/mL must be present before a discernable color develops.

Adenosine Triphosphate

Adenosine triphosphate (ATP) is a critical chemical in the metabolism of all microorganisms. Therefore, measurement of ATP can be an indicator of the number of microorganisms present. In tests, microbial cells are disrupted to release ATP, which is then reacted with luciferin and luciferase to produce visible light. This is the common reaction used by the firefly to emit light. Intensity of light produced is measured using a photometer and related to the amount of bacteria present. Some ATP from dead organisms may be present in bulk water, and free ATP measurement (where cells are not disrupted) should be used as a blank. The ATP test is simple and can be quickly conducted in the field.

The main advantage of this method is a rapid assessment of the relative number of microorganisms present. The method is quite sensitive to low levels of biological activity, and it is widely used in the food and paper industries. The major disadvantages of the method are no absolute correlations to CFU/mL from dip slide or DMA results, no indication of the type of microorganisms present, and equipment and reagents are relatively expensive.

Having data on the amount of viable and free ATP in the system is very useful, as it indicates the presence, or previous presence, of many life forms that are not easily plated. Combined with plate counts for some microbes, the ATP measurement is a valuable tool.

Online Biological Monitoring

Several methods exist for online monitoring of biological control agents, particularly halogens. These can be used for controlling halogen dosage, but may result in overfeed if halogen demand fluctuates and becomes significant.

Halogen Monitors

Analyzers are available to monitor a sample stream for halogen content. These devices automate the diethyl-p-phenylenediamine (DPD) test to measure either free or total halogen up to 5 mg/L every few minutes. Control of halogen residual may be included within this working range. Devices are reliable and accurate but are more costly than other methods, and maintenance is required due to wet chemistry of the test method.

Oxidation Reduction Potential (ORP) Monitors

ORP is a convenient, cost-effective, and reliable means to monitor and control oxidant treatment in a system. Oxidants, like halogens, produce a potential difference (voltage) between a pair of electrodes that relates to concentration of oxidant in solution. The method is sensitive to halogen concentration within normal application range for biocontrol. Temperature and pH affect the potential reading, and some industrial ORP probes automatically compensate for temperature and pH changes. ORP can be used for control of all oxidizing biocides that produce measurable levels of halogen, including organic halogen release compounds but not stabilized halogens.

Many innovations in oxidant residual monitoring have been developed that include specific measurement of undissociated hypohalous acid, chlorine dioxide, ozone, and peroxides. Additional development has also occurred around probe maintenance that improves accuracy and reliability of measurement.

Visual Inspection

Direct observation of the cooling system is a valuable monitoring method. Look at sunlit areas of the cooling system for algae (Fig. 18.19), examine fill for slime, feel system surfaces for slime, and examine pipes and exchangers when access to them is available. A great deal can be learned from simple observation.

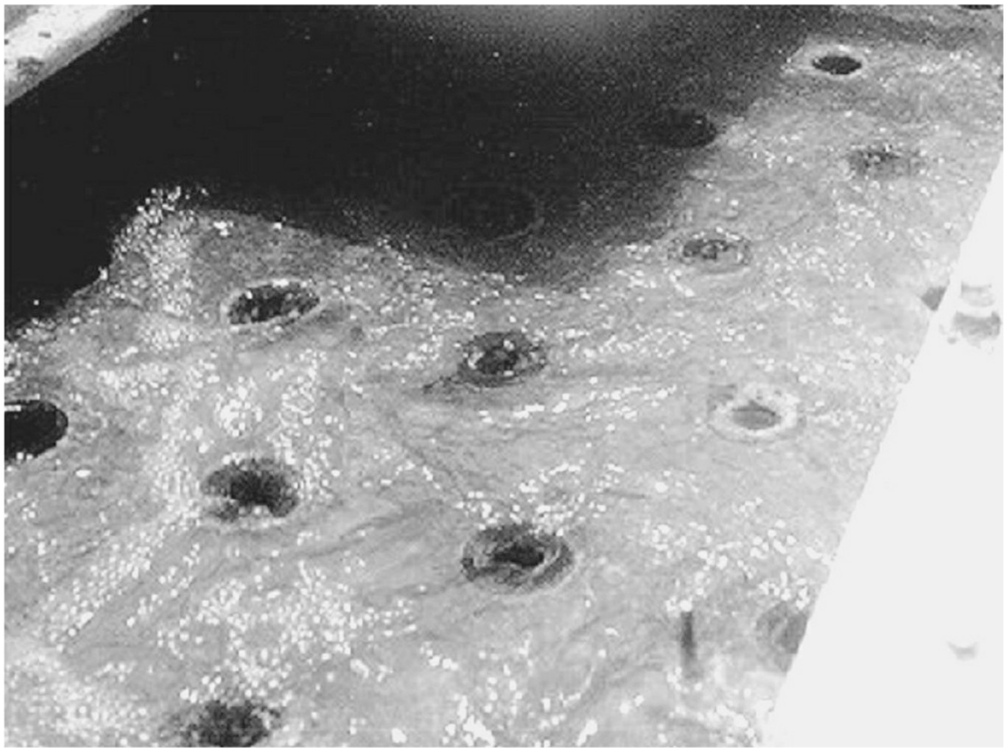


FIGURE 18.19 Open-deck cooling tower showing clean water distribution orifices and appropriate water level.

CHAPTER 19

Cooling Water Treatment and Control

Controlling deposition, corrosion, and microbial growth in cooling water systems is essential for optimizing system performance and efficiency. This chapter discusses methods to minimize deposition, corrosion, and microbial fouling in cooling systems. Chemical treatments and programs that combine both chemical treatment and control technology are covered.

Deposit Control Methods

A variety of control methods to minimize deposition are available. Water chemistry management can have a dramatic impact on scale control. Mechanical methods can affect both fouling and scale control. A wide variety of chemical inhibitors exists to improve control of scale and fouling. Most successful programs combine elements from each of these areas to improve overall plant efficiency.

Control of water chemistry and tower operation is a necessity. Examples of some areas to consider include:

- Alkalinity and pH control can minimize scale formation.
- Limiting concentration of critical ions can prevent scale formation and minimize corrosive ions like chloride and sulfate.
- Makeup water clarification or softening can reduce scale forming species or fouling materials.
- Sidestream treatment is an effective method of minimizing problems

caused by suspended matter.

- Design factors that affect water velocity, flow patterns, water and surface temperatures, heat flux, or heat exchanger surface roughness can affect scaling and fouling.
- Practices to improve system cleanliness (air rumbling of exchangers or vacuuming tower basins) can help remove suspended solids.

These factors can be controlled or modified to improve results of any treatment program.

Deposit Inhibitor Mechanisms

Inhibitors for minimizing deposits include scale inhibitors, dispersants, and surfactants. Chemical scale inhibitors can work by a variety of means: threshold inhibition, crystal modification, sequestration (chelation), or dispersion. Dispersants work by keeping suspended particles in solution. Surfactants can help prevent or remove some types of deposits. A comprehensive program may use all three chemicals for minimizing deposits in a cooling water system.

Scale Inhibitor Mechanisms

The most common scale inhibitors work by three main mechanisms:

1. Threshold inhibition is a general term where substoichiometric amounts of inhibitor (i.e., much less than 1 mg/L of inhibitor per mg/L of scaling ion) retard precipitation.
2. Crystal modification disrupts orderly growth of scale crystals, causing them to be deformed and physically weak (Figs. 19.1–19.3.) Crystal modifiers can be adsorbed on crystal growth sites, slowing kinetics of crystal growth.

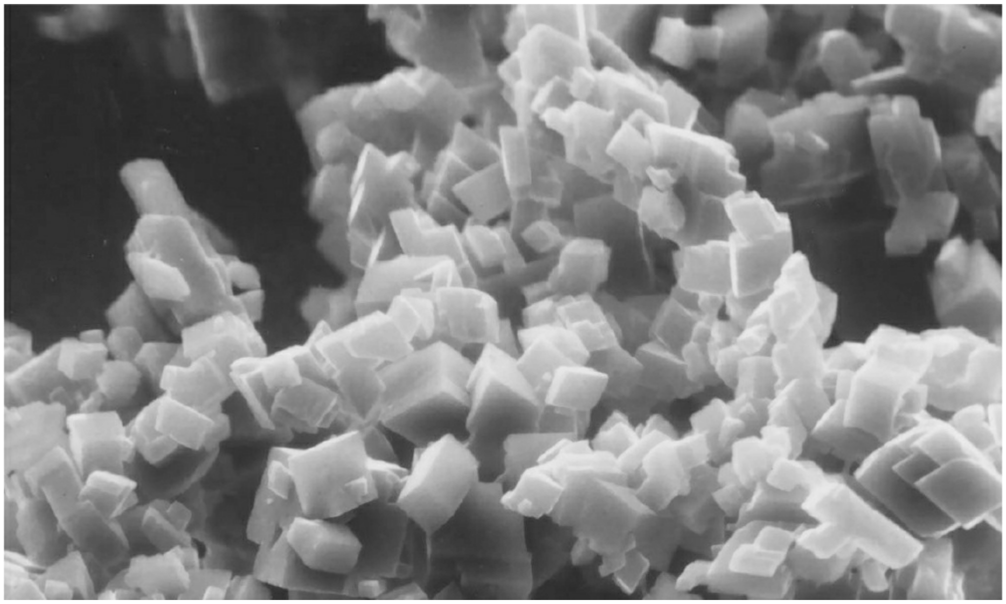


FIGURE 19.1 Untreated calcium carbonate crystals (2000×).

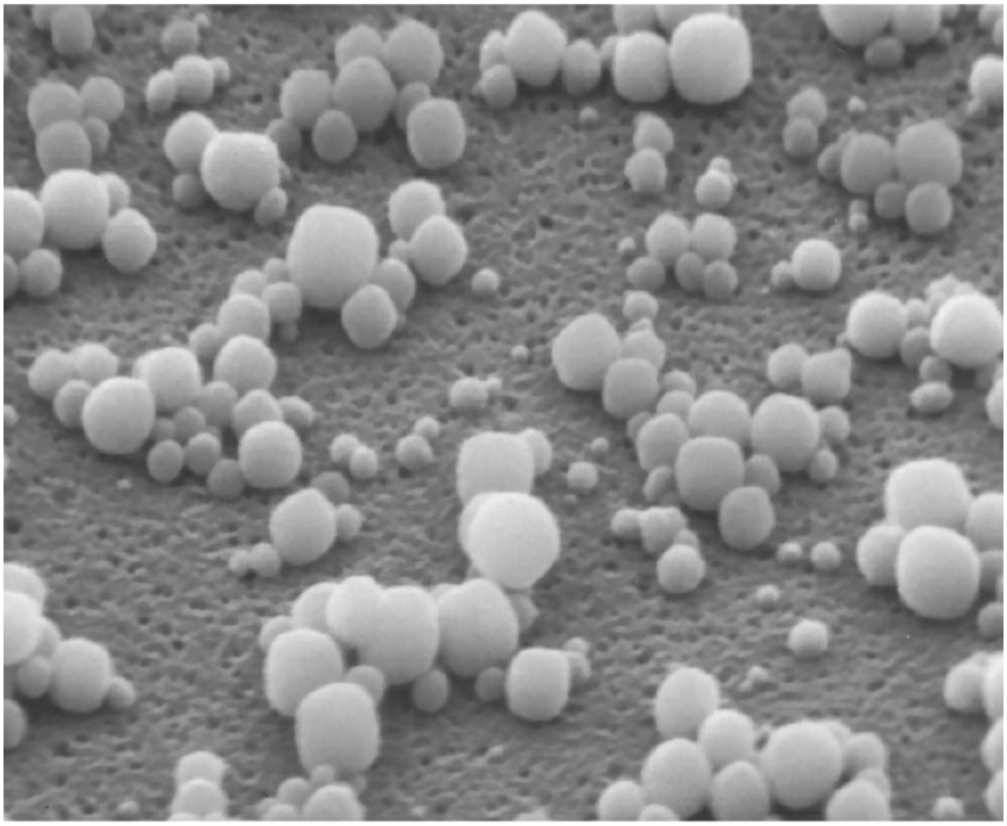


FIGURE 19.2 Calcium carbonate crystals modified by polyacrylate (2000×).

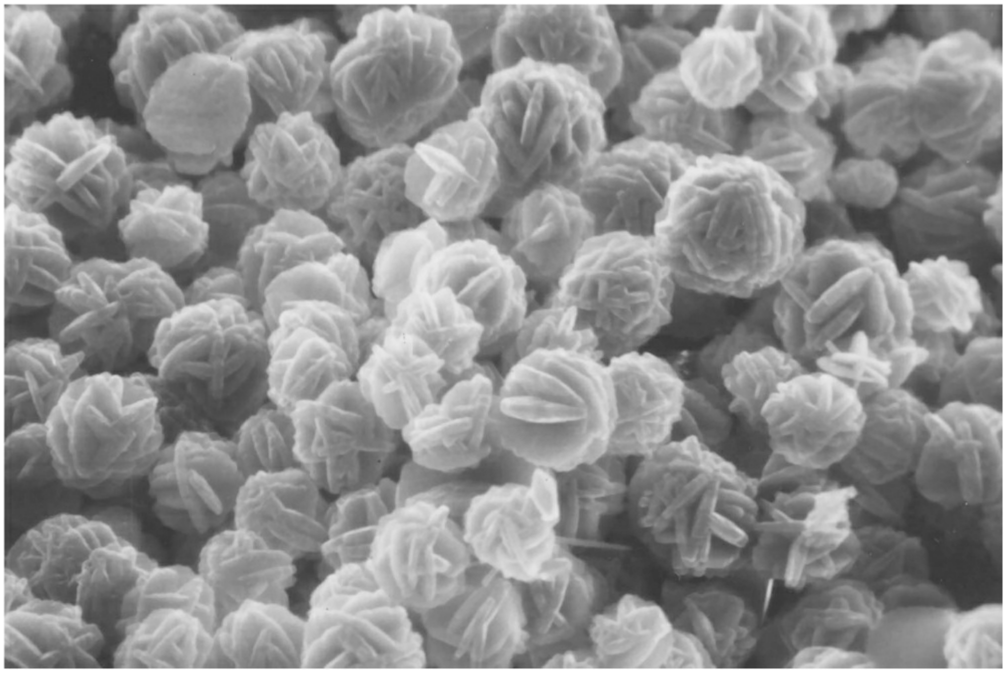


FIGURE 19.3 Calcium carbonate crystals modified by blend of phosphonate and polyacrylate (2000×).

3. Sequestrants act like chelating agents by complexing scale forming ions into a soluble ion pair to prevent deposition. It is generally a less strongly formed bond than a true chelation complex. In cooling water, polyphosphates and anionic dispersants are sequestering agents for iron, manganese, and calcium.

Other examples include dispersants and scale conditioners. Dispersants can be effective for some forms of scale. If precipitation in bulk solution occurs, particles can be dispersed by polymeric dispersants. Scale conditioners chemically modify the crystal structure of scale, by inclusion of inhibitors into the crystal lattice to form a bulky, loosely adherent, fluid type of deposit, instead of hard scale. Typical conditioning agents are lignins, tannins, and acrylate polymers.

Dispersant Mechanisms

Dispersants are highly charged synthetic polymers that prevent small particles from agglomerating into larger masses, which settle out on surfaces more easily. The mechanism of dispersion is by charge reinforcement or steric stabilization.

Dispersion by charge reinforcement increases negative electrical charge that all particles in solution have. Low molecular weight anionic polymers adsorb onto the surface of particles in water increasing the negative charge of the particle. Increased surface charge helps prevent agglomeration and settling of solids (Fig. 19.4).

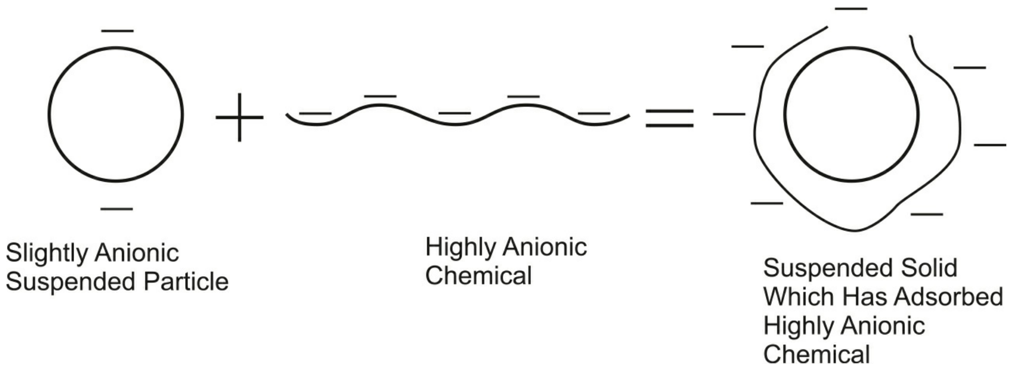


FIGURE 19.4 Suspended particle adsorbs highly anionic polymer, greatly increasing surface charge.

Adsorbed polymers on the surface of particles also prevent agglomeration by creating a physical barrier to other particles. This barrier acts like an elastic cushion that prevents particles from sticking together. This is called the steric effect and is dependent on the structure and molecular weight of the adsorbed polymer.

Generally, polymers function through both electrostatic repulsion and steric stabilization. When two particles approach each other, steric effects or charge repulsion interfere with agglomeration (Fig. 19.5). Resulting particles remain small enough that a stable suspension is produced. If two particles collide and agglomerate, particle size increases. As particle size increases, potential for deposition increases.

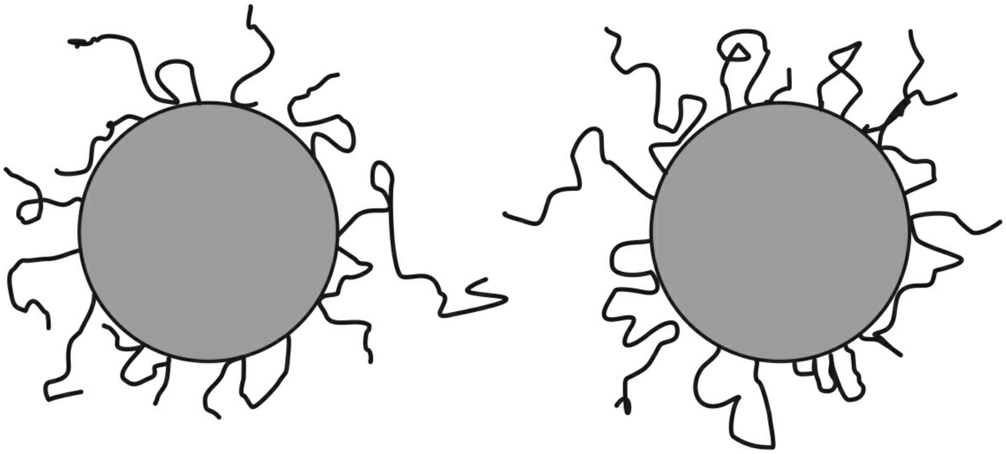


FIGURE 19.5 As particles coated with polymer approach each other, the polymer can help prevent agglomeration by charge repulsion and steric stabilization.

Surfactant Mechanisms

Surfactant molecules have a hydrophilic end (attracted by water) and a hydrophobic end (repulsed by water) (Fig. 19.6). In cooling water, the hydrophobic end is repulsed by water and forced to concentrate at the water's outer surface. This is how a surfactant reduces surface tension of water. Lower surface tension reduces energy needed to move a particle into the water phase. Particulate matter and organic materials are attracted to the hydrophobic end of the surfactant molecule and carried with recirculating water.

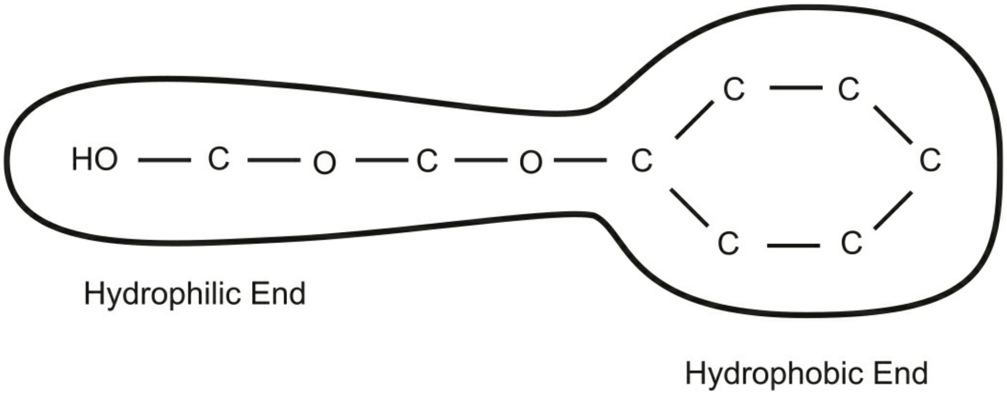
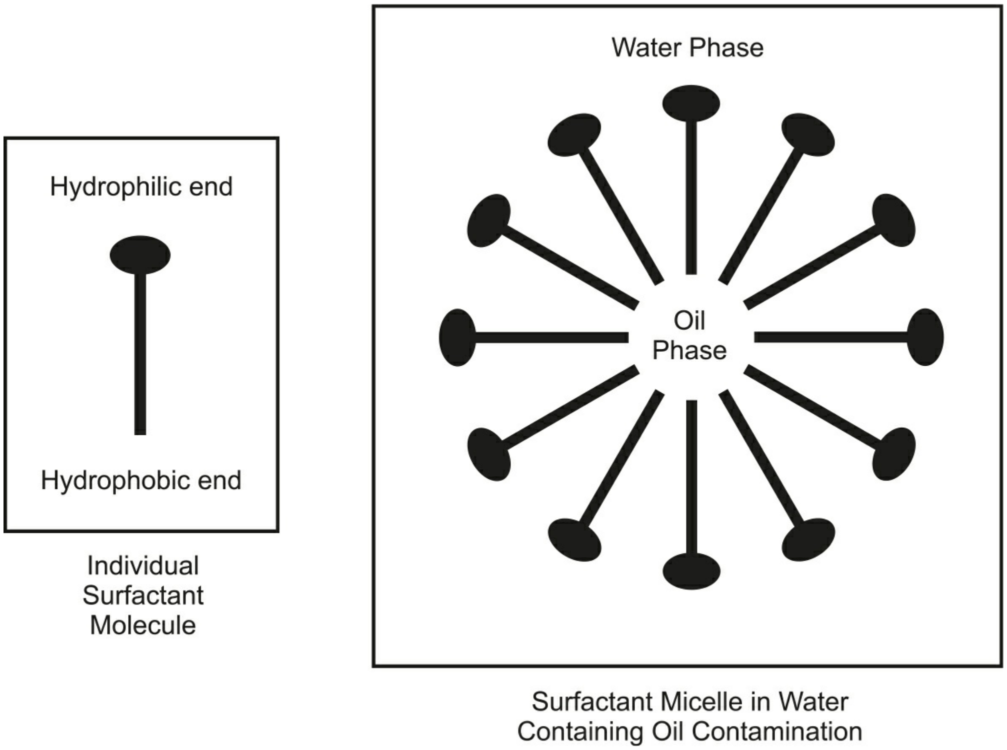


FIGURE 19.6 Typical surfactant molecule.

Surfactants form organized clusters, called micelles, around hydrocarbons in water. Micelles occur above a minimum concentration value that is characteristic of each surfactant. When water is the solvent and oil is the material to be emulsified (oil in water), the hydrophobic end is in the oil, and the hydrophilic end is in the water (Fig. 19.7). In a nonaqueous system (water in oil), the reverse is true. This emulsifying mechanism is used to remove process leaks or hydrocarbons that have fouled metal surfaces.



Individual Surfactant Molecule

Surfactant Micelle in Water Containing Oil Contamination

FIGURE 19.7 Micelles are organized clusters of surfactant molecules in solution. Oil can be emulsified and dispersed by the surfactant micelle.

Examples of Deposit Inhibitors

A wide range of chemicals exists that can help to inhibit deposition, either scale or fouling. Many types of phosphate compounds have been used as scale inhibitors for calcium carbonate ($CaCO_3$) and calcium sulfate ($CaSO_4$). Among the most successful have been the phosphonates. Examples of these include amino tris (methylene phosphonic acid) (AMP), 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP), and 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTC).

Polymers

Some polymers are strictly dispersants to prevent deposition of suspended material, and some are both scale inhibitors and dispersants. Polymers used for scale inhibition or dispersant applications are generally low molecular weight materials (1000–30 000), with a variety of negatively charged functional groups. Polymers can be either homopolymers of one monomer, or copolymers or terpolymers of two or three monomers. Copolymers and terpolymers generally give better performance than homopolymers for the same function, except for calcium carbonate scale control. Copolymers and terpolymers can be optimized for different tasks like calcium phosphate or iron stabilization. Each type of polymer has different properties and performs differently in cooling water systems.

The real benefit of these polymers is the ability to prevent deposition under high stress conditions. Polymers containing sulfonate functionality are generally best at this.

Silica Scale Inhibitors

Application of cost-effective reliable silica inhibitors has long been a goal in the water treatment industry. There are a growing number of applications in the market. Silica control is an active area of investigation and innovation in the water treatment marketplace. Even now, there are inhibitors that prevent silica scale over 200 mg/L levels in the water, and some show effectiveness up to 300 mg/L.

Polymers for Silica Inhibition A variety of polymers are marketed for silica scale control, including a copolymer of acrylic acid and allyl-hydroxy-propyl sulfonate ether (AA/AHPSE), polyepoxysuccinic acid (PESA), and alkyl epoxy carboxylate (AEC). A promising dispersant is a terpolymer of acrylic acid (AA), 2-acrylamido-2-methylpropylsulfonic acid (AMPS) and t-butylacrylamide (t-BAM). This material is expensive, but it can be effective. An example of the performance of this polymer in preventing silica scale is shown in Fig. 19.8.

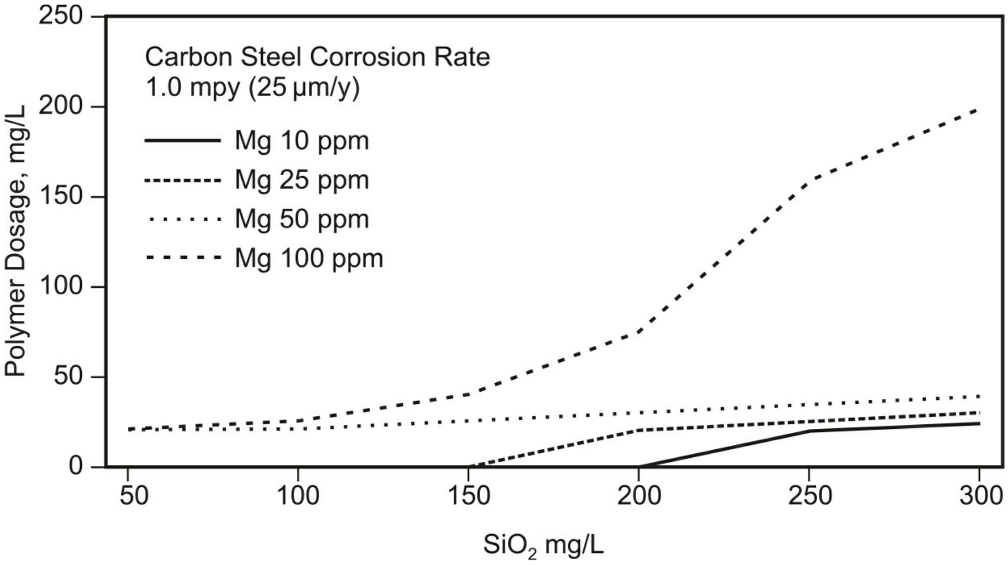


FIGURE 19.8 Dosage of AA/AMPS/t-BAM polymer needed for various silica and magnesium concentrations.

Borate Nalco developed the application of borate for maintaining soluble silica in excess of 300 mg/L in cooling water. It is fed at a high level, but is very effective. Dosage depends on silica in makeup water and desired cycles of concentration. Due to environmental discharge limits on boron, application of this technology is limited in some areas.

Surfactants

Surfactants (surface active agents) are organic chemicals with applications in cooling systems that include biodispersants, oil dispersants, and cleaning applications. Surfactants function in the following ways:

- Wetting—reduction of surface tension between two liquids or liquid and solid, so that the two materials make very good contact
- Detergency—breaking adhesion of soils to surfaces and dispersing and suspending particulate soils
- Emulsification—homogenizing grease, oil, or fat into small particles, dispersed evenly into a liquid phase (generally water) by chemical action

There are four basic types of surfactants, examples of which are shown in Fig. 19.9. Anionic surfactants (negative charge) like linear alkyl benzene sulfonate (LAS) are generally the least expensive and oldest known surfactants. However, LAS is not biodegradable, and its use is limited in some areas and countries. Nonionic surfactants (no charge) are used as dispersants and often give better performance with lower foaming than anionic surfactants. Cationic (positive charge) and amphoteric (both negative and positive charge) surfactants are primarily used in fabric softeners, bacteriostats, cosmetics, personal care products, and other specialty applications.

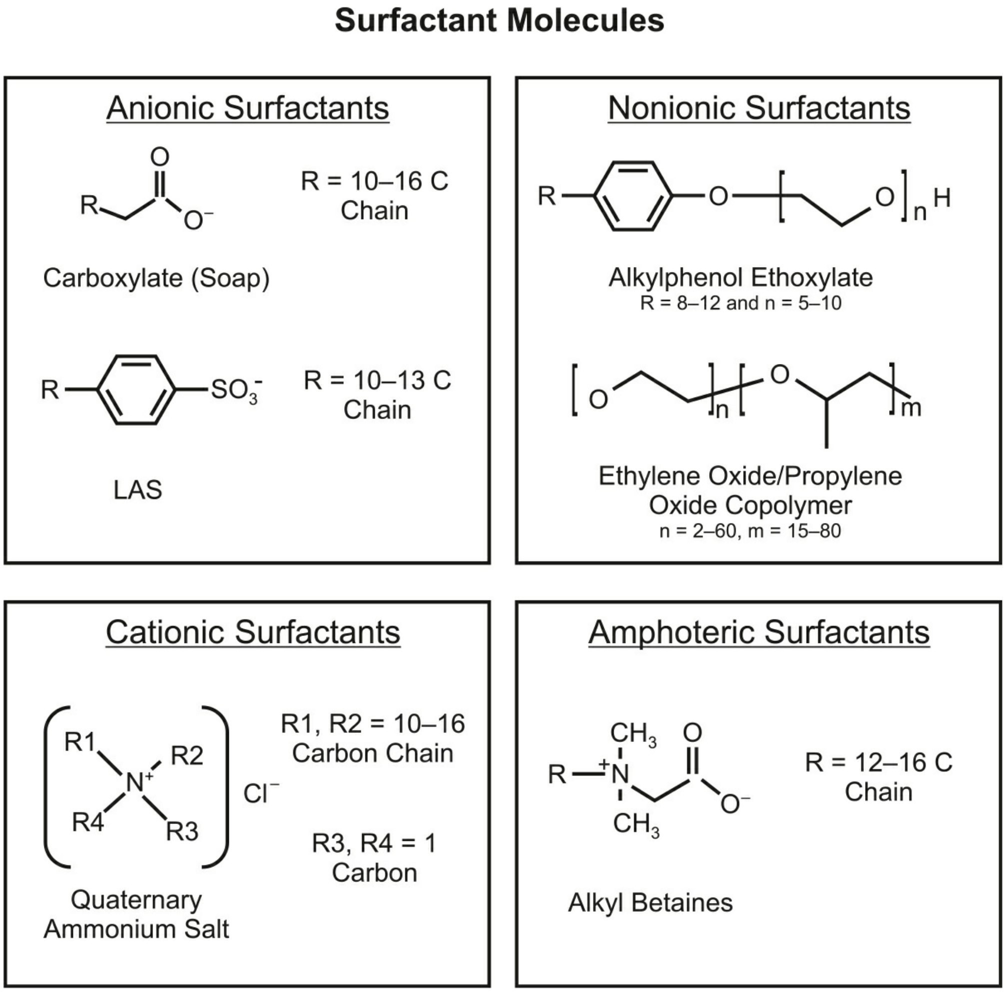


FIGURE 19.9 Structures of some common surfactants.

Surfactants can be beneficial in cooling water programs. Materials that reduce interfacial tension between water and bacterial slime layers, can help remove these deposits and make chlorination or bromination more effective. Surfactants can help emulsify oil leaks in refineries and chemical plants, keeping oil dispersed in water. Other types of surfactants can be useful in dispersing soils or suspended solids. Surfactants are not often used on a continuous basis, but may be part of a periodic cleaning program. One caution when using surfactants in cooling towers is the foam that may result. Dosage control is important to minimize foaming, and having antifoam on hand is valuable if undesirable foaming occurs.

Corrosion Control Methods

Corrosion control is a key part of maintaining a cooling water system. The corrosion problem can be the most complex to solve; thus, it is important to know all possible avenues for control. A complete solution involves combination of several possible ways to minimize corrosion. Some common methods include:

- Use of corrosion resistant materials such as stainless steel, copper-nickel alloys, and plastic.
- Applications of coatings or inert barriers such as paint, epoxy coatings, and metal cladding to separate metal from water.
- Cathodic protection, which supplies electrons to metal that would normally corrode. This turns an anodic metal (electron producer) like steel into a cathode (electron supplier), which means the steel does not corrode.
- Sacrificial anodes reduce corrosive attack by electrically coupling a more anodic metal (usually zinc, magnesium, or aluminum) to equipment metal (usually carbon steel).
- Application of chemical corrosion inhibitors as part of a complete cooling water treatment program to reduce corrosion, fouling, and microbial growth.

Knowledge of possible benefits and pitfalls of each solution is important. For example, one might think that using stainless steel in all parts of a system would be the answer to all corrosion problems. However, this would be an expensive solution. Other problems including stress corrosion cracking or pitting of stainless steel may result from high chloride concentration. Either of these could lead to more catastrophic damage than general corrosion on regular carbon steel.

Corrosion Inhibitor Mechanisms

All parts of a corrosion circuit must be completed for corrosion to proceed. This includes anodic and cathodic reactions, conduction of electrons through metal, and flow of ions in solution. Therefore, any chemical applied to water that stops one part of the corrosion reaction reduces corrosion. Chemical inhibitor classification is based on how the inhibitor affects the corrosion cell.

Chemical inhibitors, therefore, are put into four general classifications: anodic inhibitors, cathodic inhibitors, combination anodic and cathodic inhibitors (bipolar films), and film-forming inhibitors.

Anodic Corrosion Inhibitors

Anodic corrosion inhibitors function by interfering with the anodic reaction, reducing the rate of dissolution of metal into solution. For example, corroding iron produces ferrous ions and iron oxides. Anodic inhibitors function to either promote formation of protective iron oxide films, or by forming precipitates that improve characteristics of oxide films, in order to reduce both physical and chemical ion permeability. The oxide film must have physical integrity to prevent diffusion of metal ions into solution or prevent ions in solution from penetrating to the metal surface (Fig. 19.10). If the film is permeable or damaged, resulting metal loss is concentrated at the break in the film. This produces high corrosion rates at small anodic sites, and pitting results. Therefore, it is important to maintain sufficient quantities of anodic inhibitor in the system at all times to prevent pitting attack.

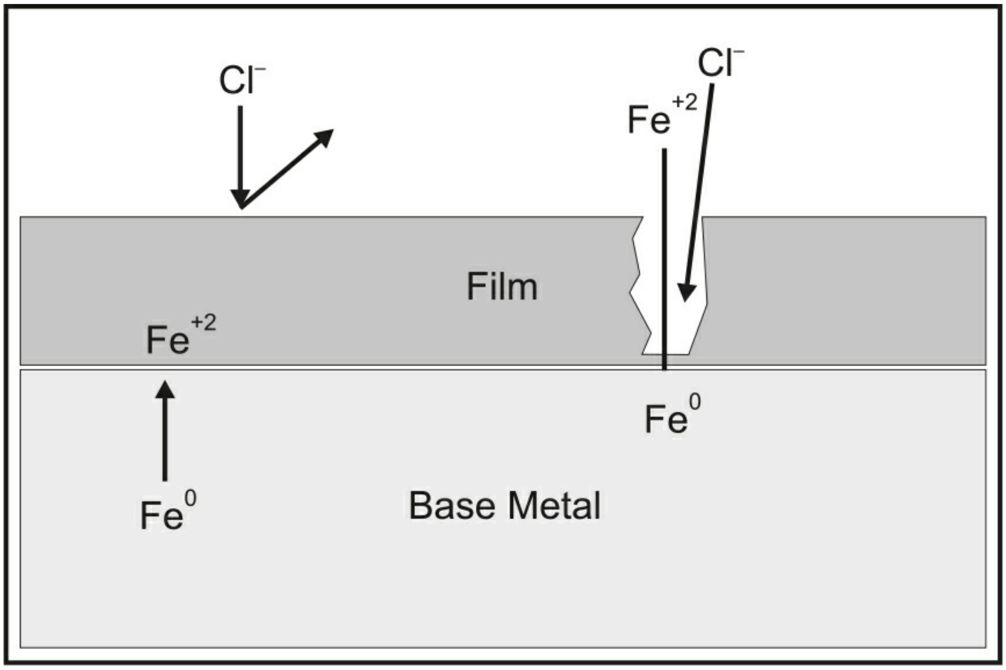


FIGURE 19.10 An effective anodic film is impermeable to both ferrous ions and aggressive ions in solution like chloride. If there are breaks in the film (right), ferrous ions can be transported into solution, and chloride can penetrate the film, increasing the corrosion rate.

Based upon the mechanism of inhibition, anodic inhibitors can be classified into two categories: oxidizing inhibitors or nonoxidizing inhibitors.

Oxidizing Anodic Inhibitors This group (of which nitrite is an example) promotes rapid oxidation of the metal surface to form a thin tightly adherent layer of metal oxides. They do not require oxygen in order to function. On steel, the protective layer is a passive film of gamma iron oxide (FeOOH). Passive films can be very thin and invisible to the unaided eye. These oxidizing anodic inhibitors are called "dangerous" inhibitors when used alone, because pitting problems can occur, if dosage drops below the passivation level.

Nonoxidizing Anodic Inhibitors The second class of anodic inhibitor is not capable of oxidizing ferrous to ferric iron, and requires the presence of oxygen to provide corrosion protection. These inhibitors function by reacting with dissolving metal ions such as ferrous (Fe^{+2}), to form an insoluble salt or complex that precipitates as a film on anodic sites (e.g., iron salts of carbonate, orthophosphate, phosphonate, or molybdate). These materials facilitate formation of an inhibiting film by catalyzing reaction of ferrous iron to ferric oxides, like gamma iron oxide, or these inhibitors chemisorb on the oxide layer, reducing ionic permeability of said layer.

Cathodic Corrosion Inhibitors

Cathodic inhibitors prevent reduction of oxygen or electron transfer at the cathode. Cathodic barrier films need physical and electrical impermeability to prevent oxygen from physically reaching the metal surface, and to prevent electron flow from the metal through the film. Both are needed to prevent oxygen reduction (Fig. 19.11).

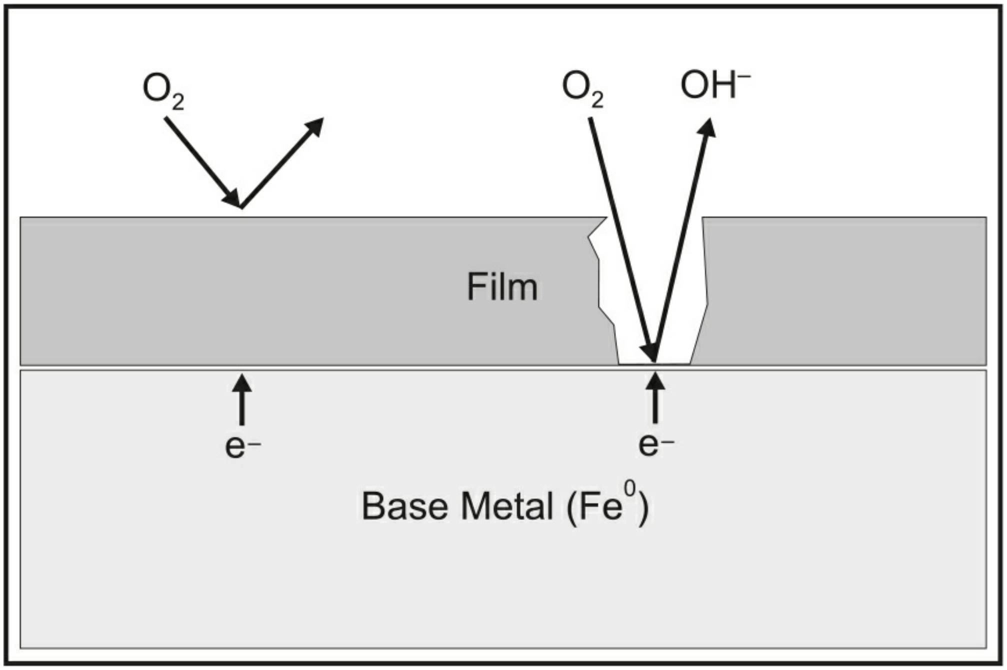
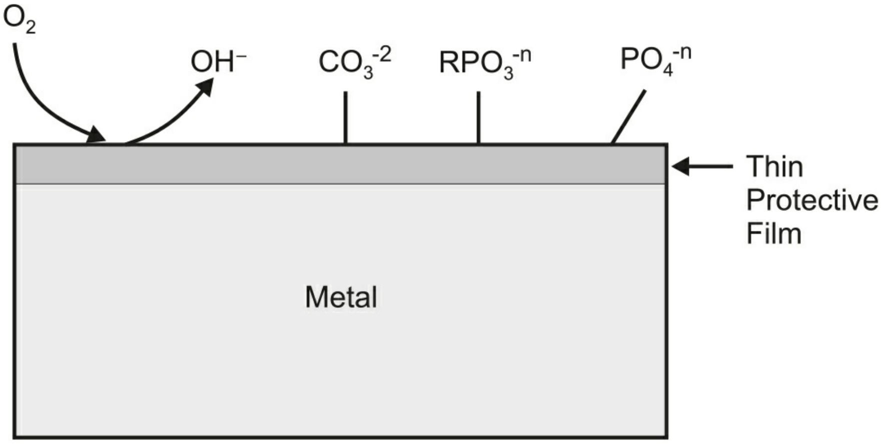


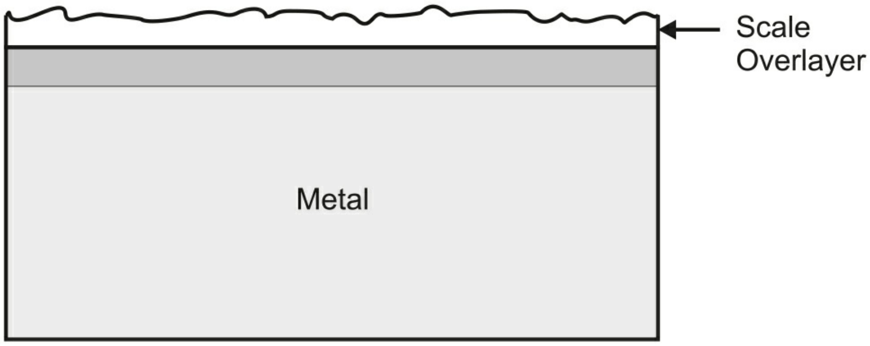
FIGURE 19.11 An effective cathodic film is impermeable to oxygen and an effective insulator for electron transfer. Breaks in the film allow oxygen penetration and reduction with electrons in the metal, increasing the corrosion rate.

Cathodic barrier films are generally catalyzed by hydroxide (OH^-) produced by the cathodic reaction. Localized high pH (measured as high as pH 10–11) at cathodic sites can precipitate various compounds and create an inhibitor film. A zinc-based inhibitor is a good example. When corrosion occurs, the OH^- ions produced decrease solubility of zinc ions in solution, and zinc hydroxide or carbonate precipitates at these high pH sites. As corrosion is reduced, formation of hydroxide decreases, and the growth of inhibiting film is reduced. These inhibitors are generally considered self-limiting film formers.

The challenge of a good cathodic inhibitor program is to allow this pH driven mechanism to occur, while preventing thermally driven precipitation of the inhibitor (Fig. 19.12). Proper polymer selection is essential in designing an inhibitor program for balanced control of pH and thermally driven precipitation. The polymer helps to prevent thermally driven precipitation, while allowing the protective pH driven mechanism to occur.



pH Driven Mechanism
- Self-limiting film
- Formation rate inversely proportional to corrosion
- Cathodic inhibition



Thermally Driven Mechanism
- Not self-limiting
- Related to thermal differential
- Total heat transfer rate reduced

FIGURE 19.12 Cathodic film formation occurs by a self-limiting pH driven mechanism. Thermally driven precipitation of scale is not self-limiting and is controlled by polymers.

Bipolar Films

Combinations of both anodic and cathodic inhibitors are sometimes called synergistic, since the combination provides lower corrosion rates than either inhibitor alone, even at high levels. Combinations can prevent problems that may occur when using only one type of inhibitor alone, such as pitting that may occur if the concentration of an anodic inhibitor is too low. Inhibitor combinations result in a bipolar film of metal oxides produced by the anodic inhibitor, and a barrier film produced by the cathodic inhibitor, simply represented by two layers on a metal surface (Fig. 19.13). The oxide layer prevents dissolution of base metal, and the barrier film prevents transfer of electrons and reduction of oxygen.

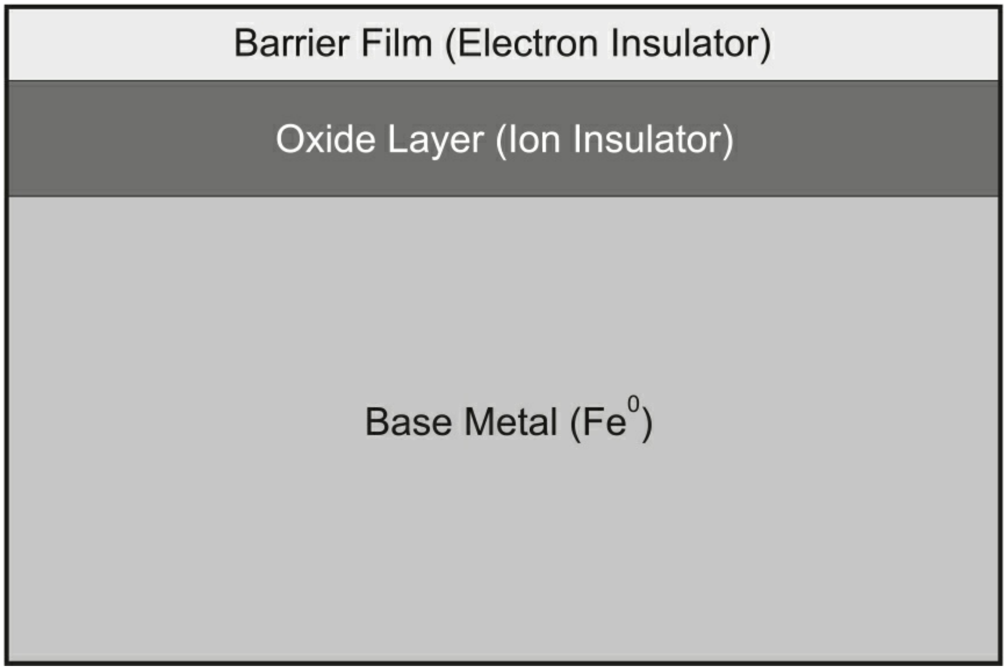


FIGURE 19.13 The strongest corrosion inhibiting films combine properties of anodic oxide layers with cathodic barrier films.

Film-Forming Inhibitors

While all inhibitors form a layer of some kind, some inhibitors produce an inhibitor film on the metal surface mostly by adsorption, which limits corrosion. This category includes organic materials that maintain a barrier between the water and metal surface to prevent corrosion. An inherent danger in the film-forming approach is that a small break in the continuous film could allow the corrosive agent to attack the unprotected area, resulting in rapid metal penetration. Therefore, filming inhibitors must be continuously fed to cooling systems to maintain the protective film. Azoles fall into this category.

Examples of Corrosion Inhibitors

An effective corrosion control program usually depends on specific inhibitors for reducing the anodic reaction, the cathodic reaction, or both. Common inhibitors used for corrosion protection in cooling water systems are shown in

Table 19.1. Most inhibitors may exhibit both anodic and cathodic characteristics, but the principal mode is primarily anodic or cathodic.

Principally Anodic	Principally Cathodic	Both Anodic and Cathodic
Nitrite	Carbonate	Azoles
Orthophosphate	Polyphosphate	Phosphonates
Bicarbonate	Zinc	Organic filming amines
Silicate		
Molybdate		

TABLE 19.1 Typical Corrosion Inhibitor Classification

A variety of anodic inhibitors exists, most of which are nonoxidizing. Their properties vary based on chemistry of their interaction with iron.

Zinc and polyphosphate are cathodic corrosion inhibitors commonly used in cooling water systems. Since they are cathodic inhibitors, they can be effective on more metals than just iron or steel. This is because interaction with the cathodic reaction (hydroxide production) is the same for all metals.

Zinc Zinc-based programs have been used for many years. A typical alkaline zinc program combines cathodic protection of zinc with anodic inhibition of orthophosphate, to operate at low zinc levels (0.5–2.5 mg/L) and pH ranging from 7 to 9. These programs use specialized polymers for stabilization of zinc in solution. Zinc is a cost-effective corrosion inhibitor and is used in many different types of applications. Corrosion inhibition is provided by positively charged soluble zinc ions (Zn^{+2}), which are attracted to the negative ionic environment at cathodic surface sites, and form a film that prevents oxygen reduction. Environmental restrictions may limit use of zinc in some applications and some regions of the world.

Polyphosphates Polyphosphates, described earlier in this chapter as stabilizers of calcium carbonate, are also corrosion inhibitors. Polyphosphates require the presence of a divalent ion such as calcium to function as a corrosion inhibitor. Calcium polyphosphate can precipitate at the cathode, due to limited solubility at the localized high pH. To effectively form calcium polyphosphate film, calcium must be present at sufficient concentration. Depending upon the polyphosphate used, the minimum concentration of calcium is typically 50 to 100 mg/L as $CaCO_3$.

Combined Anodic and Cathodic Inhibitors

Depending on water chemistry, some phosphonate (organic phosphate) scale inhibitors can function as both anodic or cathodic inhibitors. Phosphonates as corrosion inhibitors are common in all-organic treatment programs operating at highly alkaline conditions. In the anodic reaction, phosphonates catalyze oxidation of ferrous hydroxide to gamma iron oxide (FeOOH). As with orthophosphate, the presence of oxygen is required. As cathodic inhibitors, calcium phosphonates can precipitate to form a barrier film on the metal surface. The film can be a coprecipitate with calcium carbonate, depending on pH and water chemistry. The first phosphonates commonly used in these applications were AMP, HEDP, and PBTC (described earlier in this chapter for their ability to control calcium-based scale). Some phosphonates that are more effective on corrosion include PCA (phosphino-carboxylic acid) and HPA (hydroxyphosphono-acetic acid), and PSO (phosphino succinic oligomer).

PCA has a C—P—C bond instead of the C—P—O bond of more common phosphonates. Depending on structure, these can be optimized as dispersants or as corrosion inhibitors. HPA is a specific PCA that is a very effective corrosion inhibitor and has been used in all-organic programs. It is expensive and very sensitive to chlorine. It is not widely used in large cooling tower systems.

PSO was originally developed as a scale inhibitor but has excellent corrosion inhibiting properties as well. It is stable to halogens even at high dosage (up to 5 mg/L halogen). The mechanism of action is primarily cathodic, but it has anodic inhibition characteristics as dosage increases. As a cathodic inhibitor, PSO functions by precipitating a calcium-PSO or iron-PSO film, similar to pyrophosphate, at cathodic areas. Anodic function is similar to other phosphonates that work with oxygen to form gamma iron oxide. PSO yields much lower corrosion rates than other phosphonates as shown in Table 19.2.

Inhibitor	Corrosion Rate at 15 mg/L Active	Corrosion Rate at 30 mg/L Active
No inhibitor (Blank)	44 mpy (1118 μm/y)	44 mpy (1118 μm/y)
PSO	2.5 mpy (64 μm/y)	1.0 mpy (25 μm/y)
HEDP	13 mpy (330 μm/y)	8.1 mpy (206 μm/y)
AMP	9.3 mpy (236 μm/y)	16 mpy (406 μm/y)
PBTC	6.2 mpy (157 μm/y)	10 mpy (254 μm/y)

Test Conditions: 360 mg/L $CaCl_2$ (as $CaCO_3$), 200 mg/L $MgSO_4$ (as $CaCO_3$), 100 mg/L $NaHCO_3$, pH 8.4, 120°F (49°C), 160 rpm, 16-hour immersion.

TABLE 19.2 Corrosion Inhibition Screening Tests of Phosphonates

Film-Forming Inhibitors

Typical film-forming inhibitors include azoles and thiazoles applied to reduce copper and copper alloy corrosion. These organic compounds are chemisorbed onto the metal surface and form thin protective films. In addition to corrosion protection, they form complexes with soluble copper in solution and prevent redeposition of copper metal onto other surfaces. Azoles are incorporated into a wide range of programs for both closed and open systems.

The most common azoles are benzotriazole (BZT) and tolyltriazole (TT or TTA). BZT and TT are both relatively stable under conditions of typical cooling water conditions. Alkyl benzotriazoles have been proposed to form more stable, longer lasting films. Two examples are butyl benzotriazole (BBT) and pentoxy benzotriazole (POBT).

Chloro-tolyltriazole has been used as a halogen resistant azole (HRA). This material was introduced to minimize problems with TT application in heavily chlorinated systems. Chlorination of the benzene ring (Fig. 19.14) in HRA minimizes reaction of chlorine with nitrogen atoms in the azole ring.

One of the earliest azoles used was mercaptobenzothiazole (MBT), but it is not used widely today. MBT (Fig. 19.15) provides excellent copper corrosion inhibition. The molecule reacts with copper surfaces via the –SH group to form a barrier film. This copper corrosion inhibitor is the fastest film former of the azoles. It is useful well above the boiling point of water. Microorganisms degrade the molecule rapidly, while halogens and oxygen oxidize the –SH group rapidly. MBT finds widespread use primarily in closed and once through cooling water systems, where these degradation pathways are less problematic.

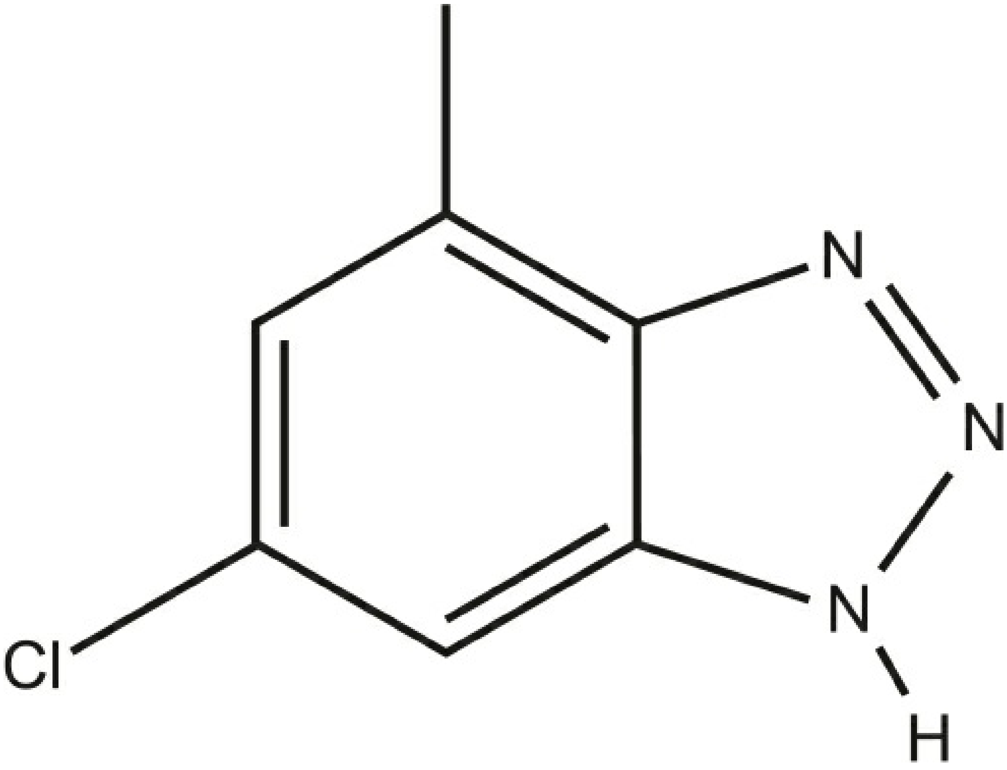


FIGURE 19.14 Structure of chloro-tolyltriazole.

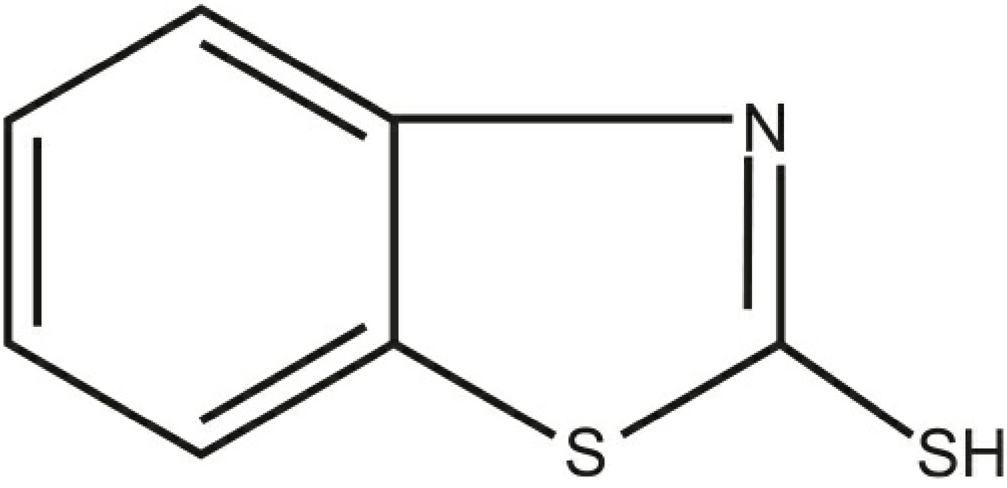


FIGURE 19.15 Structure of mercaptobenzothiazole.

Biological Control Methods

Control of biological growth in cooling systems requires a management approach that considers the mechanical aspects, chemical characteristics, and operation of the system. Many of these factors were described in Chap. 17.

This section covers chemical control of microorganisms in cooling systems. Because of biocide toxicity to other organisms in the environment, any control method that minimizes the amount of biocide used is valuable. In the future, less toxic methods of control will be more desirable.

Control of microbiological contamination is not simply choosing the right biocide, rather it is a program to control biofouling. This program requires in-depth understanding of the cooling system, and includes taking measures to exclude harmful microorganisms and environmental and process contaminants. The program also uses biocides, and dispersants, as well as filtration to remove suspended solids, and must include a firm plan, to monitor effectiveness and reduce biological diversity.

Oxidizing Biocides

Oxidizing biocides include chlorine, bromine, chlorine dioxide, ozone, chlorine or bromine slow-release compounds, stabilized halogens, peroxide and peroxyacetic acid. Although there are differences among these materials, their primary mode of action is to oxidize compounds in microorganisms. Chlorination is an oxidizing reaction; however, we need to note that oxidation is not always chlorination. This insight will be useful later in this section. No organism has ever been shown to develop resistance to an oxidizing biocide. Oxidizers are effective against all types of microorganisms in cooling systems, including bacteria, fungi, algae, and yeast.

Chlorine and Hypochlorite

Generally, chlorine is supplied as chlorine gas (Cl_2), dissolved in sodium hydroxide as sodium hypochlorite (NaOCl), or as a solid like calcium hypochlorite [$Ca(OCl)_2$]. When chlorine gas is dissolved in water, it produces hypochlorous acid (HOCl) and hydrochloric acid (HCl) as in Eq. (19.1). Hypochlorous acid dissociates in water to produce hypochlorite ion (OCl^-) and hydrogen ion (H^+) as shown in Eq. (19.2). Sodium hypochlorite or calcium hypochlorite produce HOCl when diluted in cooling water [the reverse reaction in Eq. (19.2)]. Hypochlorous acid is the active biocide when either chlorine gas or hypochlorite is introduced into water. Hypochlorite ion is a less effective biocide than HOCL.

$$Cl_2 + H_2O \rightarrow HCl + HOCl \tag{19.1}$$

$$HOCl \rightleftharpoons H^+ + OCl^- \tag{19.2}$$

System pH affects the amount of HOCl present and thus biocidal effectiveness of chlorine in a cooling water system. As pH increases, percent of hypochlorous acid decreases as shown in Fig. 19.16. As the curves indicate, the percent of hypochlorous acid is limited above pH 8. As temperature increases, the amount of HOCl at a given pH decreases. Therefore, chlorine is most effective in systems that operate near neutral or slightly alkaline pH.

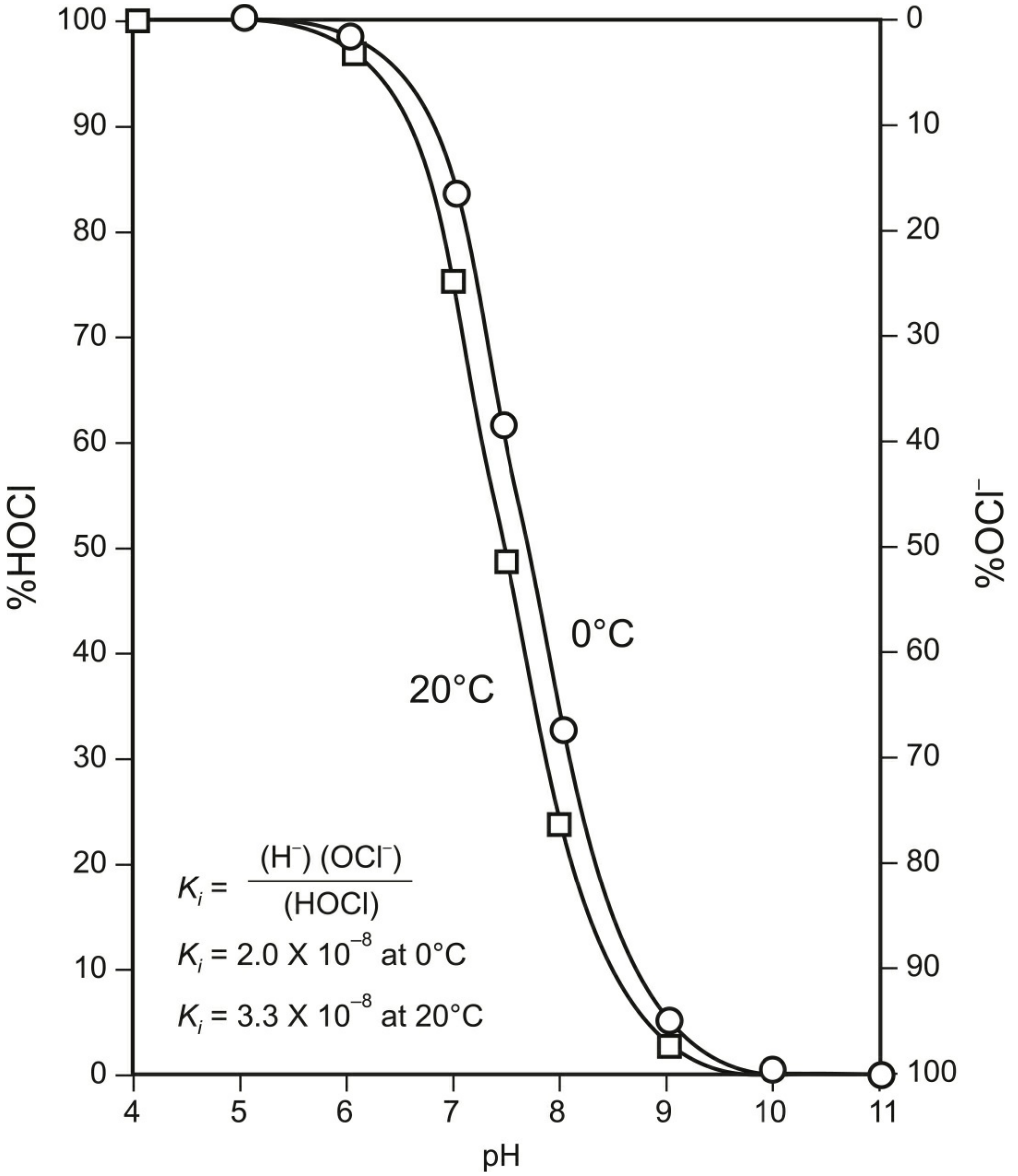


FIGURE 19.16 Dissociation of hypochlorous acid versus pH.

Hypochlorous acid can also be produced electrochemically from a sodium chloride solution. This process is sometimes more expensive than purchasing sodium hypochlorite since equipment, maintenance, and power costs may be significant. This method is often used in situations where seawater is available, or sodium hypochlorite is difficult to obtain, or environmental concerns regarding storage of chemicals is paramount.

Chlorine-Release Compounds and Stabilized Halogens

A variety of organic compounds releases hypochlorous acid when dissolved in water. These chemicals are easier or safer to feed than gaseous or liquid chlorine compounds. Organic compounds that are available, vary in stability, product form, cost, and chlorine-release mechanism. One chlorine-release compound that has relatively good stability and safety characteristics is sodium dichloroisocyanurate dihydrate. Figure 19.17 shows the reactions that release hypochlorous acid when added to water. Another stabilized chlorine compound is produced when sodium sulfamate is added to a bleach solution. The chlorosulfamate formed in this process serves to release HOCl in water [Eq. (19.3)].

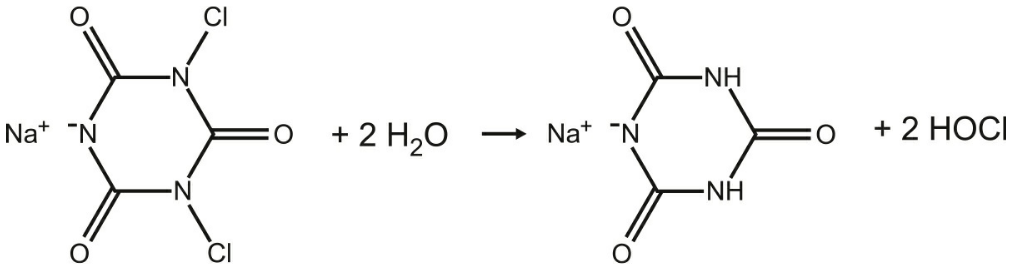


FIGURE 19.17 Chlorine-release mechanism of sodium dichloroisocyanurate dihydrate.

$$ClHNSO_3Na + H_2O \rightarrow HOCl + H_2NSO_3Na \qquad (19.3)$$

Bromine

Bromine undergoes the same reactions as chlorine. Bromine dissolves in water to form hypobromous acid (HOBr), which dissociates to give an equilibrium mixture of hypobromous acid and hypobromite ion (OBr^-). HOBr is similar in biocidal activity to HOCl. The major advantage of bromine over chlorine is that more HOBr is available at higher pH and temperature (Fig. 19.18). Therefore, in systems that operate at pH above 7.5, bromine is a more effective biocide than chlorine.

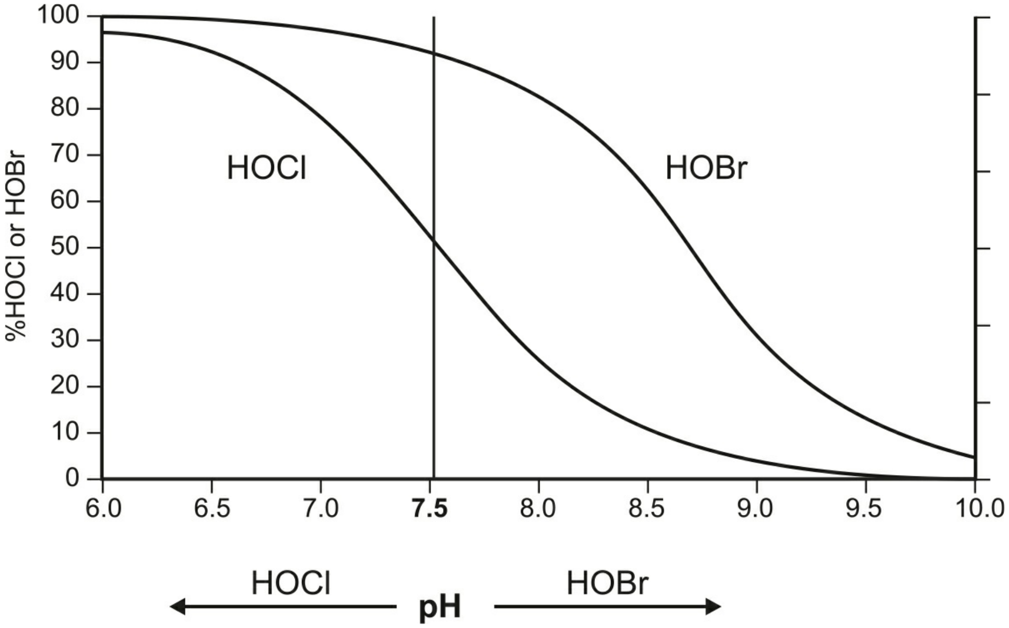


FIGURE 19.18 More active HOBr is available at any given cooling water pH compared to active HOCl.

Bromine is a liquid at normal ambient pressure and temperature and not a gas like chlorine. Handling and feeding liquid bromine to cooling systems creates safety concerns. In addition, concentrated sodium hypobromite (NaOBr) solutions are not stable because NaOBr decomposes rather quickly. Three safe ways to use bromine biocides are:

1. On-site HOBr generation can be cost-effectively done by mixing a solution of sodium bromide and a chlorine source such as sodium hypochlorite. The reaction to produce HOBr is very fast, and varying ratios of chlorine to bromine actives can be produced.
2. Bromine-release compounds like bromo chloro dimethyl hydantoin (BCDMH), which generates both HOBr and HOCl in water, can be used. Solid BCDMH requires a dry feed system, using makeup water to dissolve the product.
3. Stabilized bromine products involve a combination of NaOBr and a stabilizer. The result is a stable liquid product that is relatively safe and easy to feed to cooling systems. In cooling water, the stabilizer releases bromine as HOBr is consumed.

Non-Biological Halogen Consumption Chlorine and bromine can be consumed by other materials in cooling water that reduce availability for biological control. Ammonia, organics, and even some treatment components react with chlorine and bromine.

Reaction of chlorine with ammonia in cooling water, or in on-site generators, to form chloramines (combined chlorine) is one of the most common reactions. Depending on the amount of chlorination and ammonia concentration, monochloramine [Eq. (19.4)], dichloramine [Eq. (19.5)], or trichloramine [Eq. (19.6)] may be formed. Chloramines are less effective biocides and do not kill as quickly as HOCl.

$$\mathrm{HOCl} + \mathrm{NH_3} \rightleftharpoons \mathrm{H_2NCl} + \mathrm{H_2O} \tag{19.4}$$

$$\mathrm{HOCl} + \mathrm{H_2NCl} \rightleftharpoons \mathrm{HNCl_2} + \mathrm{H_2O} \tag{19.5}$$

$$\mathrm{HOCl} + \mathrm{HNCl_2} \rightleftharpoons \mathrm{NCl_3} + \mathrm{H_2O} \tag{19.6}$$

Cooling water treatment components can also react with chlorine. Phosphonates used as corrosion and scale inhibitors along with some azoles used for copper alloy corrosion protection can react with halogens. Some chlorinated azole compounds are volatile and can be stripped from water passing over the cooling tower. Reaction of chlorine with organic contaminants produces nonvolatile chlorinated organics, commonly called adsorbable organic halides (AOX), (adsorbable onto activated carbon). AOX is environmentally undesirable, since a number of halogenated hydrocarbons are toxic.

Chlorine Dioxide

Chlorine dioxide (ClO_2) provides excellent microbial control. Advantages and disadvantages are shown in Table 19.3. ClO_2 must be generated on-site by chemical or electrochemical methods, although systems with relatively low demand can be treated with available low concentration liquid products. The most common production methods of on-site generation are reaction of sodium chlorite ($NaClO_2$) with one of several acids [Eq. (19.7)], reaction of sodium chlorate with acid (in the presence of a reducing agent), or the reaction of sodium chlorite with chlorine or bleach [Eq. (19.8)].

Advantages of Chlorine Dioxide	Disadvantages of Chlorine Dioxide
Effective biocide Activity does not decrease at high pH Does not react with ammonia or amines Works well in high chlorine demand systems Does not react significantly with organics to produce AOX	Generally generated on-site, except for limited volumes Training and monitoring costs are significant Cost of production ranges from moderate to high Volatile and easily stripped from open systems Handling reactants is a safety concern

TABLE 19.3 Chlorine Dioxide Considerations for Cooling Systems

$$5NaClO_2 + 4HCl \rightarrow 4ClO_2 + 5NaCl + 2H_2O \tag{19.7}$$

$$2NaClO_2 + Cl_2 \rightarrow 2ClO_2 + 2NaCl \tag{19.8}$$

Sodium chlorite can also be converted electrochemically to ClO_2 in a continuous process. However, compared to chemical methods, equipment and maintenance costs can be high.

Peroxides

Hydrogen peroxide (H_2O_2) and peracetic acid (CH_3CO_3H) are sometimes used as biocides. Hydrogen peroxide is a very strong oxidant with well-known antimicrobial properties, but it can be consumed in many ways in cooling water (meaning it reacts with almost anything capable of being oxidized, thus high doses may be required). It is not persistent, and often requires multiple feed points to achieve results. Therefore, it has often shown poor performance in preventing microbial fouling. H_2O_2 has several environmental advantages, including no AOX formation, no reaction with amines, and end products are water (H_2O) and oxygen (O_2).

Peracetic acid (PAA) dissociates in water to produce hydrogen peroxide and acetic acid (CH_3CO_2H) [Eq.(19.9)]. PAA has potential as a cooling water biocide since it is a powerful oxidant (second only to ozone), and H_2O_2 contributes some capability. It is effective as high as pH 9.5, but optimum activity is achieved below pH 8.6. PAA has similar advantages to H_2O_2; main disadvantages are high cost and safety concerns of the concentrated product.

$$CH_3CO_3H + H_2O \rightleftharpoons H_2O_2 + CH_3CO_2H \tag{19.9}$$

Ozone

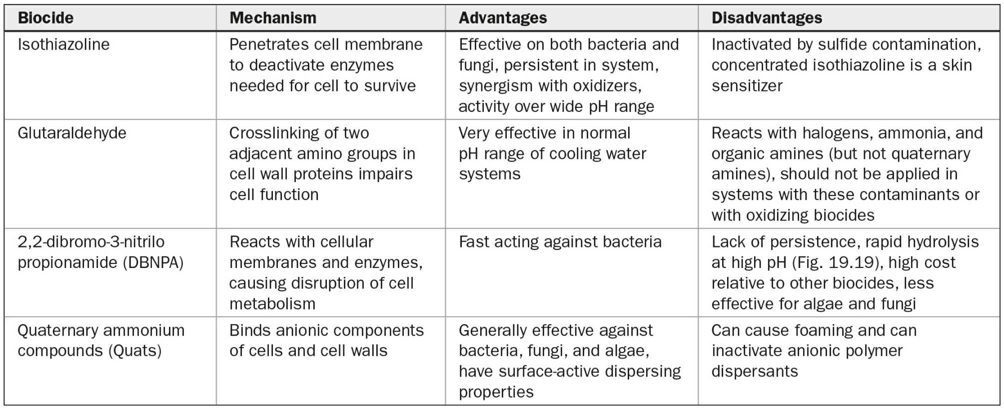
Ozone (O_3) is produced by passing oxygen or air through a corona discharge electric field. It readily dissolves in water and is a strong oxidant with several potential benefits. Ozone is one of the strongest oxidizers known, meaning it reacts with almost anything that can be oxidized, therefore resulting in high feedrate. Ozone can be an effective biocide and offers potential for being convenient, safe, and environmentally friendly. It is generated on-site, and there is no inventory of hazardous biocides. If applied properly, ozone is totally consumed in the cooling system, and ozone does not produce halogenated organics (AOX). Therefore, little or no discharge of any toxic chemicals occurs.

Ozone has important disadvantages, which have limited its application as a cooling water biocide. The half-life of ozone in cooling water is very short, and it is difficult to ensure that ozone reaches all areas of the system. As with peroxide, multiple feed points are often required. Ozone generators are expensive, and maintenance costs are high. Cost can be several times the annual water treatment chemical cost for a given system. Ozone reacts with many organics, and it can degrade components of the cooling system. Finally, ozone can increase metal corrosion rates and remove zinc from alloys.

Use of ozone has been proposed periodically as a total treatment option for cooling towers. Ozone is claimed to provide control of deposition, corrosion, and microbial fouling, sometimes while operating with zero intentional blowdown. The foundation of the claim is that if surfaces are kept clean and free of biofouling, prevention of scale, corrosion, and fouling is easier. However, if low corrosion occurs in ozone treated systems, it is most probably due to high alkalinity and pH that results when water is concentrated. Research has shown that ozone has no effect on precipitation of mineral scale and does not affect crystal morphology. Any minimization of scale on heat exchangers in ozone treated systems is again due to operating conditions and not ozone. After long use, scale may build up in the tower fill (low-flow area) rather than on heat exchangers (high-flow areas). Thus, observation that ozone is preventing scale and corrosion is more perception than reality.

Nonoxidizing Biocides

This is a large class of organic compounds that interfere with metabolism of microorganisms, inactivate cellular enzymes, bind cellular proteins, or disrupt cell walls. Biocides for cooling water are typically organic sulfur, nitrogen, chlorine, or bromine compounds. Unlike oxidizing biocides, nonoxidizers are most effective when applied in slug dosages. Many nonoxidizing biocides exhibit activity only toward bacteria, fungi, or algae and not all three. The pH of water has a dramatic influence on specificity and activity of each biocide. There is a wide range of compounds available, a few of which are described in Table 19.4.



Biocide	Mechanism	Advantages	Disadvantages
Isothiazoline	Penetrates cell membrane to deactivate enzymes needed for cell to survive	Effective on both bacteria and fungi, persistent in system, synergism with oxidizers, activity over wide pH range	Inactivated by sulfide contamination, concentrated isothiazoline is a skin sensitizer
Glutaraldehyde	Crosslinking of two adjacent amino groups in cell wall proteins impairs cell function	Very effective in normal pH range of cooling water systems	Reacts with halogens, ammonia, and organic amines (but not quaternary amines), should not be applied in systems with these contaminants or with oxidizing biocides
2,2-dibromo-3-nitrilo propionamide (DBNPA)	Reacts with cellular membranes and enzymes, causing disruption of cell metabolism	Fast acting against bacteria	Lack of persistence, rapid hydrolysis at high pH (Fig. 19.19), high cost relative to other biocides, less effective for algae and fungi
Quaternary ammonium compounds (Quats)	Binds anionic components of cells and cell walls	Generally effective against bacteria, fungi, and algae, have surface-active dispersing properties	Can cause foaming and can inactivate anionic polymer dispersants

TABLE 19.4 Examples of Some Nonoxidizing Biocides

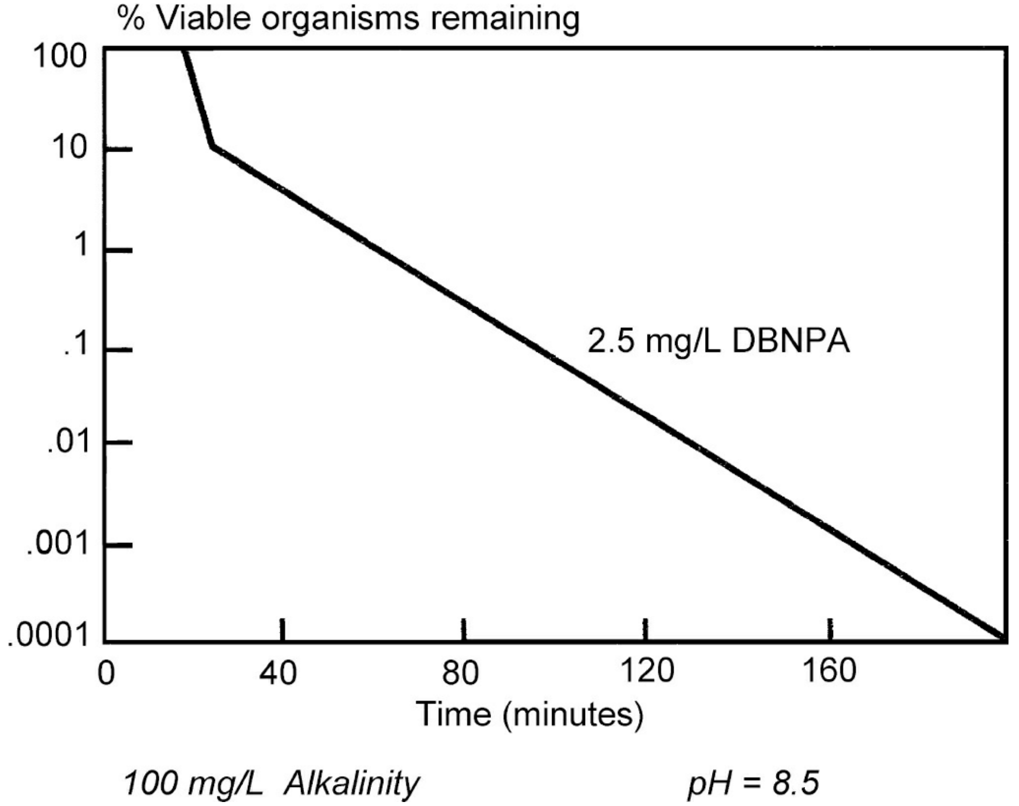


FIGURE 19.19 Efficacy of DBNPA at pH 8.5.

Algaecides

Algae are metabolically and structurally different from bacteria and often are more difficult to control with common biocides. Terbuthylazine is used specifically as an algaecide. This material interferes with photosynthesis and is very effective at low dosages against algae. However, it has no effect on non-photosynthetic microorganisms (bacteria or fungi). Up to two weeks is needed for control of algae. Terbuthylazine is much more effective when used for prevention rather than controlling existing algae problems.

Copper sulfate has long been used in water to kill or prevent algae growth. The apparent action of copper (as Cu^{+2}) on algae, is blocking transport of oxygen through cell membranes, leading to death. Inner cell protoplasm is released, giving off a characteristic odor. When copper sulfate is added to algae-laden water, algae are killed almost instantly, but considerable time may be required for disappearance of dead plants and associated foul odors. At normal dosages, copper sulfate is also effective against bacteria such as *Gallionella*, which causes iron deposits and “red water.” This product is useful for algae control in ponds but must not be used for cooling water systems because of galvanic corrosion that copper ions can cause on mild steel.

Biodispersants and Biodetergents

Biodispersants and biodetergents can improve cooling system microbial control and are an important aspect of complete biocontrol programs. These products do not kill microorganisms but help break up biofilms and suspend bacteria in water, so that they are more readily killed by biocides. Dispersants may prevent or delay attachment of microorganisms to heat transfer surfaces. The primary characteristic of biodispersants is their ability in maintaining clean system surfaces.

Biodispersants and biodetergents are typically nonionic surfactants, though some anionic surfactants are used. They are usually used in conjunction with oxidizing and nonoxidizing biocides to enhance effectiveness. They can be used with all open recirculating and once through system treatments including corrosion inhibitors, scale inhibitors, biocides, and dispersants. They are effective over a wide pH range and are thermally stable at typical cooling water temperatures. As with any surfactant, overfeed of biodispersants can result in foaming and require application of a defoamer. However, use of antifoam can reduce effectiveness of the biodispersant.

Macrofouling Control

Macrofouling attachment of mollusks to piping and other surfaces of a cooling system was described in Chap. 5. The many physical and chemical approaches to mollusk control can generally be divided into methods that prevent infestation of mollusks, or eradicate mollusks once they have grown in a system (Table 19.5). Prevention methods must be applied during the time when mollusks spawn, producing free-floating veligers that can be killed more easily than adult mollusks. Eradication involves killing and removing adult mollusks from a system.

Method	Advantages	Disadvantages
Eradication	Treatment needed only 1–3 times per year Potentially lower chemical cost	Under-deposit corrosion can occur where mollusks attach to system Potentially higher maintenance cost to remove mollusk shells Mollusk shells cause flow restriction
Prevention	No mollusk shells to remove Lower under-deposit corrosion potential (fewer mollusks in system) Generally helps to provide better overall biocontrol in system	Potentially higher chemical cost Must treat more often, generally throughout warm weather months Potentially higher capital cost for feed and detoxification equipment

TABLE 19.5 Comparison of Macrofouling Control Methods

Eradication can involve killing mollusks with biocides, but shells that plug the system must be removed by physical methods. Thermal shock can achieve 100% mortality of most mussels when water temperature of 104°F (40°C) is held for 30 minutes. Unfortunately, most facilities are not configured to apply thermal treatment, with the exception of some electric power generating plants.

Both oxidizing and nonoxidizing biocides are used for either prevention or eradication of macrofouling. Chlorine, bromine, chlorine dioxide, and ozone have all been used, with chlorine being most common. Disadvantages of chlorine are mainly environmental concerns and its corrosive nature. Dehalogenation may be required before discharge. The most cost-effective nonoxidizing biocides are quaternary ammonium compounds (quats). These compounds are toxic to many aquatic organisms (like fish), and removal from discharge water by adsorption on clay may be needed.

Amine salts of carboxylic acids have been used with success. One amine/acid combination uses *N,N*-dimethylalkyl amine and endothall (a dicarboxylic acid). The amine is not a quaternary ammonium compound, and it does not have a permanent positively charged nitrogen. Because of this, *N,N*-dimethylalkyl amine has lower water solubility than quaternary ammonium compounds. This limited solubility makes this type of amine a "film former" that coats surfaces in a system. The advantage this offers is that detoxification of the discharge water with clay is not necessary, since the active compound is depleted from water quickly.

Cooling Water Treatment Programs

Most cooling water treatment products contain combinations of cathodic and anodic inhibitors along with scale inhibitors and dispersants. These products, used in combination with biocontrol chemistry, comprise a complete approach to system treatment. Tolerance to fluctuations of system control parameters, such as pH or conductivity, can be very valuable in a treatment program. In the event of severe upsets, the ability of a treatment program to recover quickly when conditions return to normal, is essential. While every program offers different performance in this regard, combinations of anodic and cathodic inhibitors generally provide better performance.

An optimum treatment program generally can be selected for a given system, based on system parameters and water chemistry. Once the program is applied, proper monitoring and control are required for success.

Stabilized Phosphate Programs

These programs are a blend of orthophosphate, polyphosphate, and phosphonates that provide corrosion inhibition for mild steel. Stabilized phosphate programs rely on orthophosphate for anodic inhibition and polyphosphate for cathodic inhibition. Phosphonates prevent calcium carbonate scale, and one of the triazoles is generally included for copper corrosion protection. The key to success depends on special polymers that can stabilize calcium phosphate in cooling water systems.

Stabilized phosphate programs typically operate at 6 to 15 mg/L orthophosphate (PO_4) and up to 20 mg/L total phosphate concentration. Use of softened water and/or low alkalinity can require even higher phosphate residuals. Close control of system pH is required in the range of 6.8 to 8.5 for optimum corrosion and scale control. Therefore, acid is often fed for pH control. Often, simply lowering pH with acid can provide for calcium carbonate scale control, allowing higher cycles to be run, even with a phosphate program. However, even at this moderate pH, calcium phosphate is insoluble, and a calcium phosphate stabilizing polymer must be included.

This program requires calcium for corrosion inhibition and is subject to pitting problems in soft water. Stabilized phosphate programs require good control of pH, calcium concentration, phosphate dosage, and the ratio of orthophosphate to polyphosphate in the cooling system. Stabilized phosphate programs are not suitable for use when high soluble iron is found in makeup water or in systems with a long holding time index. Some regions or countries have strict phosphate discharge limitations that prevent use of traditional stabilized phosphate programs.

All-Organic Programs

These products are designed to provide corrosion inhibition, scale control, and dispersancy without any inorganic corrosion inhibitors like zinc or phosphate. Typical all-organic products are a combination of phosphonates, triazole, and stabilizing polymer. Anodic and cathodic inhibition is provided by the phosphonates, assisted by alkalinity from operating at high pH (> 8.5). Phosphonates provide calcium carbonate scale prevention, and the polymer prevents excessive precipitation of calcium phosphate. Both calcium and alkalinity are required for optimum performance.

An advantage of all-organic programs is that acid for pH control is not typically used. Control of chlorination is equally important to the success of all-organic programs. High free chlorine residuals (> 0.5 mg/L) degrade some phosphonates to orthophosphate, increasing potential for calcium phosphate deposition. As a result, control of product dosage, alkalinity, concentration ratio, and chlorine residuals are very important to the success of this program.

Alkaline Zinc Programs

Zinc can be combined with orthophosphate, phosphonates, or polyphosphate (or mixtures of these) for corrosion protection. The same polymers that are often used for stabilized phosphate or all-organic programs, are used to stabilize zinc in cooling water. These programs can operate at alkaline conditions up to pH 9, because polymers provide zinc and phosphate stabilization. Phosphonates function as scale inhibitors as well as help with corrosion inhibition. Most programs include one of the triazoles for copper corrosion inhibition.

One of the best combinations is zinc, orthophosphate, and triazole, which is generally applied at alkaline conditions. This combination provides cathodic protection from zinc and primarily anodic protection from orthophosphate. Strong cathodic inhibition provided by zinc allows this program to work in very soft water, where stabilized phosphate does not perform as well.

Alkaline Phosphate Programs

In some areas, environmental restrictions allow phosphate for corrosion control, but not the high levels of a traditional stabilized phosphate program. Some facilities do not allow acid for pH control or zinc for corrosion control. In these cases, an alkaline phosphate program may be applicable, because of operation at lower phosphate levels and higher pH and alkalinity. Original programs were a combination of phosphonate, orthophosphate or polyphosphate, triazole, and phosphate stabilizing polymer. Other programs may use phosphonates (organic phosphates), giving the advantage of lower phosphate levels. Organic phosphates like PSO can provide corrosion and scale inhibition. Alkalinity in cooling water provides some buffer capacity in the event of pH swings. The PSO/orthophosphate combination can operate over a wide pH window.

Molybdate Programs

Molybdate is used mainly as a very effective corrosion inhibitor in closed loops, at high residual levels. However, it had been also used in open recirculating tower systems sparingly due to high costs. It has been used most often in combination with other corrosion inhibitors or used at high levels. Molybdate has shown beneficial properties for reducing localized or pitting corrosion. Most molybdate programs use dosages of 5 to 20 mg/L of molybdate in cooling tower systems. This may be combined with orthophosphate or zinc at up to 5 mg/L applied dosage. Phosphonates are used for scale inhibition, and polymers are included to prevent precipitation of phosphate and zinc. Combinations with zinc or phosphate can function at lower pH, calcium, and alkalinity like an alkaline zinc program. Other combinations such as molybdate and phosphonate can be used under more alkaline conditions, similar to an all-organic program.

Non-Phosphorous Programs

Some countries have effluent restrictions that strictly limit phosphate discharge or even tax a company based on its phosphate discharge. For this reason, non-phosphorous (non-P) programs are needed; however, they are not yet widely used. Non-P programs are typically based on polymers for scale and deposit control with zinc or molybdate for corrosion control. Polymers can include simple polyacrylates, which provide $CaCO_3$ scale inhibition, and copolymers or terpolymers for zinc stabilization. Water chemistry and system operating conditions depend on the combination of inhibitors in the programs. In general, $CaCO_3$ scaling stress (pH, temperature, calcium, and alkalinity) must be lower than when using conventional phosphonate programs. Corrosion capabilities depend on levels of zinc or molybdate (or both) that are fed to the system. In general, corrosivity of system water must be lower than with an alkaline zinc program.

Nonchemical Devices

No discussion of cooling system treatment would be complete without inclusion of nonchemical devices. These include magnetic devices, electrostatic devices, frequency generators, and a host of other nonchemical treatment methods. The lure of these devices is obvious; install a simple mechanical device and never worry about chemical treatment again. However, if it does not work, cleaning and repair costs to remove corrosion and scale deposits can far outweigh potential savings.

Magnetic fields can have effects on ions and particles in solution, but translating this to corrosion and scale prevention is an example of a pseudoscientific leap of faith. This is exemplified by many different explanations of how magnetic devices condition water, and the many different designs available from different manufacturers. For example, some say that electromagnets are necessary, while some use permanent magnets. Some devices spin water as it goes though the magnet, and some must pass water over magnets at specific angles. Some say the magnetic effect “lasts for up to five days,” and others indicate the water must be “retreated” on each pass through the system. The variety of explanations does not give much confidence that the true effect is known and understood.

The majority of nonchemical devices claim to prevent mineral scale, and some claim to prevent corrosion. This is certainly not true of magnetic devices, as these are proven to cause corrosion. Most do not claim to prevent biofouling and are often used with biocides. Some electrolytic devices that release copper or silver ions, which are toxic to microbial organisms, can help minimize biofouling, but devices that work by magnetic, electrostatic, or radio frequency, do not have this effect. Prevention of mineral scale is claimed to occur by modifying ions in solution, so that they are attracted to each other rather than to system piping. Other explanations are that the charge on scale particles is modified, so that amorphous particles rather than hard crystalline scale are formed. Either way, the “small, amorphous, scale particles” can supposedly be flushed from the system rather than deposited on heat exchange surfaces.

Complicating this picture is that several university studies conducted on magnetic water treatment do show that there can be a fundamental effect of magnetism on ions and particles in solution. Many of these studies appear in technical journals rather than peer-reviewed scientific journals. In many cases, experiments are not repeated or cannot be repeated (like the infamous “cold fusion” experiments in 1989). In addition, these studies of fundamental effects on ions and particles do not prove that magnetic treatment can prevent scale in cooling tower systems. Thus, any user of nonchemical devices should still monitor system performance on a regular frequency to evaluate system status.

SECTION 3.4

Applications—Water Safety for Building Water Systems

CHAPTER 20

Legionella and Legionellosis

Most organisms that live and grow in engineered water systems do not represent a significant health hazard to humans. The previous chapter discussed the health-related risk due to *Legionella* and other opportunistic waterborne pathogens if engineered water systems are not properly managed. Of particular concern is *Legionella pneumophilia* serogroup 1, which causes over 90% of the legionellosis outbreaks that occur worldwide. Unfortunately, this potentially pathogenic pneumonia-causing bacterium can sometimes be found in engineered water systems. *Legionella pneumophilia* is a member of a genus, or group of bacteria, called *Legionella* (Fig. 20.1). Engineered water systems can become contaminated with *Legionella* because these bacteria are common in many natural waterways, like lakes and rivers. Other human-made or engineered water systems can also be contaminated by *Legionella*. For example, many types of systems including spas, decorative fountains, and even potable hot water systems may be contaminated with *Legionella*. All of these systems can provide adequate environmental conditions for these bacteria to survive and grow. *Legionella* cause a disease called legionellosis that includes both Legionnaires' disease and Pontiac fever.

FIGURE 20.1 *Legionella pneumophila* bacteria first isolated by Charles Shepard and Joseph McDade of the CDC in 1977. (*Courtesy of US Department of Health and Human Services, Source: National Library of Medicine, Images from History of the Public Health Service.*)

The purpose of this chapter is to provide basic information on *Legionella* bacteria, the diseases caused by these bacteria, the factors that increase risk of infection from these bacteria, and sources of risk. Understanding these characteristics will help a facility or utilities manager determine the best course of action for managing risk from systems like cooling towers and potable water systems. Aspects of monitoring, assessing the risks, regulations relating to *Legionella* management, and treatment are covered in Chap. 21 on Water Management Programs for Engineered Water Systems.

The Disease

Pneumonia is an ancient disease of the lungs that is caused by both viral and bacterial sources. *Legionella* bacteria were first identified as a cause of a pneumonia-like disease in humans in 1976. Since being discovered, *Legionella* bacteria, the systems that may harbor the bacteria, and the conditions that encourage *Legionella* growth, have been studied in great depth.

Legionellosis is the term used to describe all infections caused by *Legionella* bacteria. This includes both Legionnaires' disease and Pontiac fever (described later). Legionnaires' disease is the more serious illness. Although large outbreaks involving several hundred people have occurred, Legionnaires' disease is uncommon. This disease must be taken seriously because the consequences can be severe and the disease is deemed preventable.

The number of legionellosis cases that occur annually are difficult to determine. Even when diagnosed, the disease is sometimes not reported, so the total number of actual infections is probably higher than statistics suggest. Larger outbreaks are more commonly reported because of the publicity surrounding the disease. Sporadic cases may go unreported. The Centers for Disease Control and Prevention (CDC) states that between 8000 and 18 000 people are hospitalized in the United States each year due to legionellosis. The European Union (EU) estimates the occurrence of legionellosis varies from 120 cases per million people, depending on the reporting procedures of individual European countries. Both the CDC and EU estimate the actual number of cases to be higher because some cases are not reported. Projecting the CDC value to the world population would suggest that there might be as many as several hundred thousand cases of Legionnaires' disease each year. Most of the cases are probably sporadic, involving only a few people. About 20% of the cases are acquired during hospitalization, and 10 to 20% can be linked to larger outbreaks. The mortality rate is 5 to 20% of people who contract the disease, and the susceptibility of the individual to the disease is an important component of both contracting the disease and mortality (Bartram, et al.).

Legionnaires' Disease Symptoms

Legionnaires' disease is a serious infection of the respiratory system. Legionnaires' disease may be difficult to differentiate from other types of bacterial pneumonia because the symptoms are similar. Individuals will have high fever, chills, headache, fatigue, and muscle pain. A dry cough develops, and most patients suffer breathing difficulty. Some patients also develop diarrhea or vomiting and can become confused or delirious. The disease will develop in 2 to 10 days after exposure to the bacteria and can persist for weeks or be fatal if not treated properly. When properly diagnosed and detected early, Legionnaires' disease can be treated with antibiotics. In those people who survive a severe infection, weakness, poor memory, and fatigue, can last for months after the pneumonia symptoms are gone. Lung damage can persist for even longer periods after severe infection.

While the symptoms can be clearly described, only a qualified healthcare professional can diagnose legionellosis. Anyone with these types of symptoms should seek immediate attention by a physician.

Susceptibility

According to the CDC, most people exposed to the bacteria do not become ill. Healthy people under 20 years of age generally do not become ill, even if exposed to *Legionella pneumophila*. Healthy people over 20 years of age can catch the disease, but healthy people generally have a lower risk of death due to the disease. In most cases, only a small percentage of those exposed to the bacteria will develop disease symptoms. According to the World Health Organization (WHO), 0.1 to 5.0% of the general population may catch Legionnaires' disease if exposed to the bacteria (Bartram, et al.).

The physical condition and health of the person exposed to *Legionella* bacteria are important components of whether or not the individual develops the disease. Legionnaires' disease occurs most often in elderly people and those that have some common risk factors. The age factor varies considerably in different references from people over 40 years to people over 65 years. Examples of additional risk factors include smoking, cancer or suppressed immune system, lung or respiratory disease, chronic restrictive lung disease (like emphysema), and liver or kidney failure (Bartram, et al.) and heart disease. This is not necessarily a complete list of risk factors and only a qualified medical practitioner can properly assess the susceptibility of an individual to *Legionella* bacteria. Data from certain regions also suggests that men are more likely to contract Legionnaires' disease than women and that contracting the disease through person-to-person contact is unlikely.

Pontiac Fever Variant

Pontiac fever is a less serious infection that causes a flu-like illness. This disease is rarely fatal even though Pontiac fever is caused by *Legionella* bacteria. It is named from an outbreak that occurred in Pontiac, Michigan in 1968. The symptoms of Pontiac fever are headache, fatigue, fever, joint and muscle pain, and in some cases, nausea, vomiting, and coughing. No deaths have been attributed to Pontiac fever. This disease is often considered similar to influenza rather than pneumonia.

As opposed to Legionnaires' disease, Pontiac fever can affect healthy people and as many as 95% of exposed individuals may catch the disease. Typically, the incubation period is 13 days, and the disease lasts typically only 25 days. Treatment is generally not necessary for recovery from Pontiac fever (Bartram, et al.).

First Identified Outbreak

The first time *Legionella* was recognized as the cause of disease occurred after the convention of the American Legion in Philadelphia, Pennsylvania in 1976. Many attendees and workers at the hotel where the convention was held suffered from a serious pneumonia-like illness. Before the outbreak ended, 221 people became ill, many were hospitalized, and 34 died (Edelstein, et al.). The specific cause of the disease outbreak was not immediately identified. About six months later, scientists identified the cause to be a specific bacterium. *Legionella pneumophila* was the genus and species name given to the bacterium. The disease was called Legionnaires' disease, because of the connection to the outbreak at the American Legion convention.

A possible source of the bacteria for this outbreak was the heating, ventilation, and air-conditioning (HVAC) system in the hotel. The true source could not be identified, because the bacteria were not identified until six months after the outbreak. Those that became ill had apparently inhaled droplets of contaminated water from some part of the HVAC system. The droplets could have come from the condensate on the cooling units in the rooms or possibly drift from the cooling tower on the roof of the hotel.

Drift is an aerosol of water droplets that is carried out of the cooling tower by the airflow as illustrated in Fig. 20.2. Refer to Chap. 14 on Cooling System Dynamics for more on drift. Cooling towers are designed to evaporate water for cooling. The evaporated water vapor will not carry the bacteria. Depending on the effectiveness of the drift eliminators in the tower, varying amounts of drift will be carried out of a cooling tower by the airflow. If the bacteria in the drift were carried into the person's lung by these small water droplets, the bacteria could grow and multiply in the lungs of susceptible individuals, causing the disease.

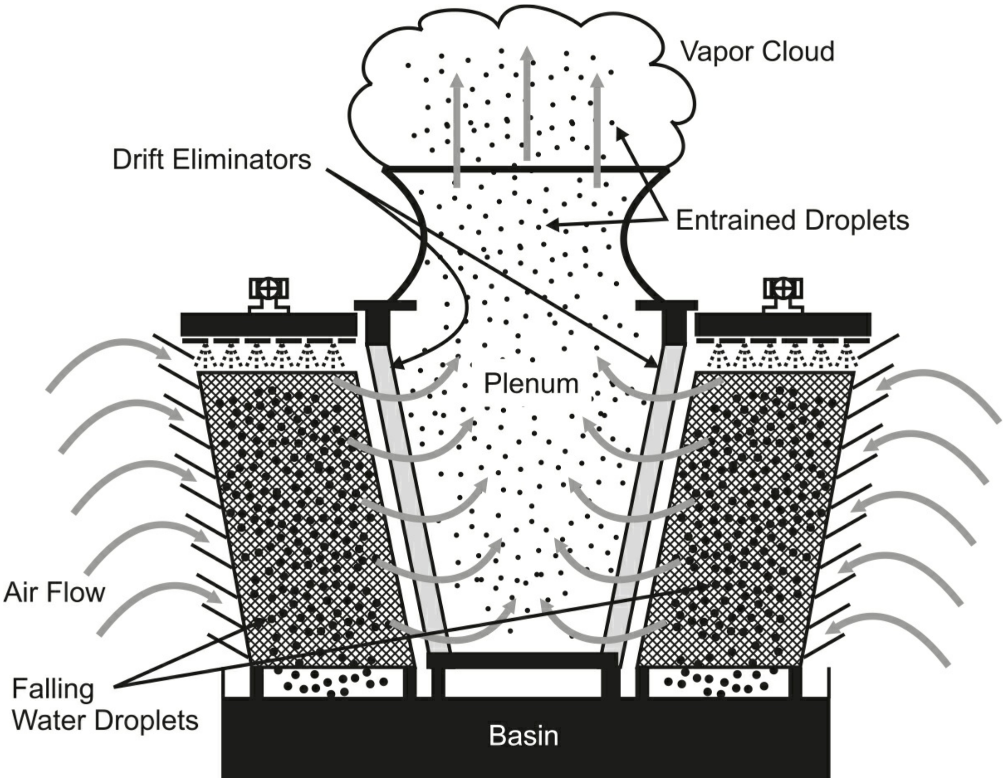


FIGURE 20.2 The small water droplets that escape the drift eliminators are known as drift. If *Legionella* bacteria are present in the tower water, the drift can carry the bacteria out of the cooling tower. The condensed vapor cloud from the evaporated water is not drift and does not carry the bacteria.

Other Outbreaks

Previously unsolved pneumonia outbreaks were studied after *Legionella pneumophila* was first identified from the Legionnaires' convention outbreak in 1976. Specimens had been saved from the 1940s through the 1960s from these unknown cases of pneumonia. Special testing showed that several of these saved cultures contained *Legionella*, and those illnesses had been Legionnaires' disease.

Since 1976, numerous sporadic cases of Legionnaires' disease have been occurring each year, with larger outbreaks involving many people occurring periodically. Outbreaks have happened in different parts of the world involving contaminated water from different types of systems, not just cooling towers. The following are examples of some outbreaks to illustrate the types of water systems that may be involved.

In 1996, about four people in two groups of tourists staying in campsites in Spain and southern France developed Legionnaires' disease. There were no cooling towers or spas at these facilities. *Legionella pneumophila* serogroup

1 was found in the hot water system of one of the shower facilities. While a clinical connection could not be established for this site as the cause, the hot water system was the most likely source of an aerosol capable of carrying *Legionella pneumophila* into a person's lungs (Infuso, A. et al.).

The Westfriese Flora (flower show) is held annually in Bovenkarspel in the northwest of the Netherlands. The show features agricultural and consumer exhibits. The February 1999 show attracted 80 000 visitors. Subsequently, 181 people who had visited during the second half of the show developed pneumonia from *Legionella*, and 21 died. A water sample from one of the whirlpool spas in the consumer products exhibits contained *Legionella pneumophila*. This water was shown to be the source of the bacteria by comparing cultures derived from the patients to cultures from the water (den Boer, J. W. et al.).

About 90 people were diagnosed with Legionnaires' disease out of about 50 000 people, who attended a trade fair in Kapellen, Belgium in November 1999. Almost all of the people who became ill required hospitalization, and five of the patients died from the disease. Testing showed that the length of time spent in particular areas in the exhibition hall was probably associated with the disease. The sources of the bacteria, found in that part of the exhibition hall, were a whirlpool and a fountain that were contaminated with *Legionella* (de Schrijver, K. et al.).

A rather unique individual case occurred in California in the 1990s where a dentist died from legionellosis. Subsequent investigations showed high levels of the same *Legionella* species in the dental unit water system at his office (Atlas, R. M., et al.).

Other large outbreaks have occurred in other places, including an outbreak at the opening of an aquarium in Melbourne, Australia in 2000. A community outbreak in Murcia, Spain in 2001 involved over 700 people who developed illness. The source was not identified, but thought to be a cooling tower near the center of town. In 2014 industrial cooling towers were thought to be linked to a significant outbreak in Portugal whilst in New York City in July of 2015 over 124 cases and 12 deaths were attributed to a cooling tower located on the roof of a hotel in the Bronx.

Thus, *Legionella* can be found in a variety of human-made water systems that use natural water sources, municipal treated drinking water, or may be contaminated with windblown dust.

The Bacteria

There are many members of the genus *Legionella*, also referred to in the plural form, *Legionellae*. *Legionellae* are rod-shaped, aerobic bacteria found widely in nature as well as in many human-made water systems (Fig. 20.3). *Legionella* can be determined by a variety of methods, including standard plating techniques and specific antibody testing. Figure 20.4 shows an example of an agar plate with *Legionella* bacteria. The genus *Legionella* has over 50 different species according to the WHO. *Legionella pneumophila* is just one of the species that is known. Twenty *Legionella* species have been reported to cause human pneumonia. The remaining 30+ species have been isolated only from water sources. All but two of the *Legionella* species that have been isolated from patients have also been found in the environment.

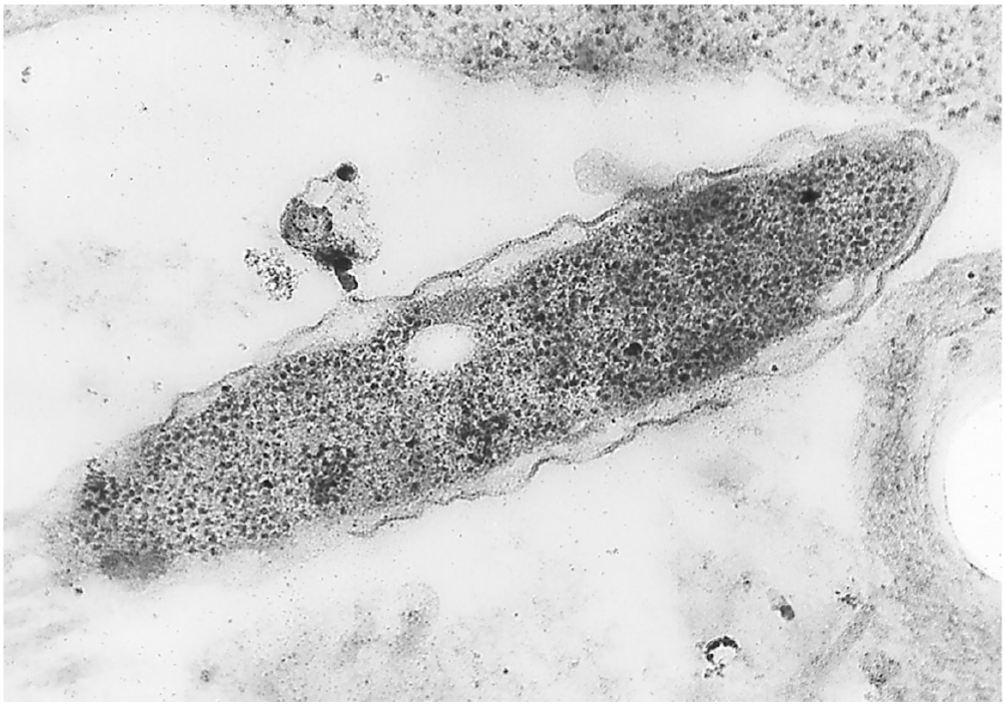


FIGURE 20.3 *Legionella* cells are rod-shaped bacteria as shown in this transmission electron micrograph of a *Legionella pneumophila* bacterium, magnified approximately 119 500×. (*Courtesy of CDC Public Health Image Library*.)

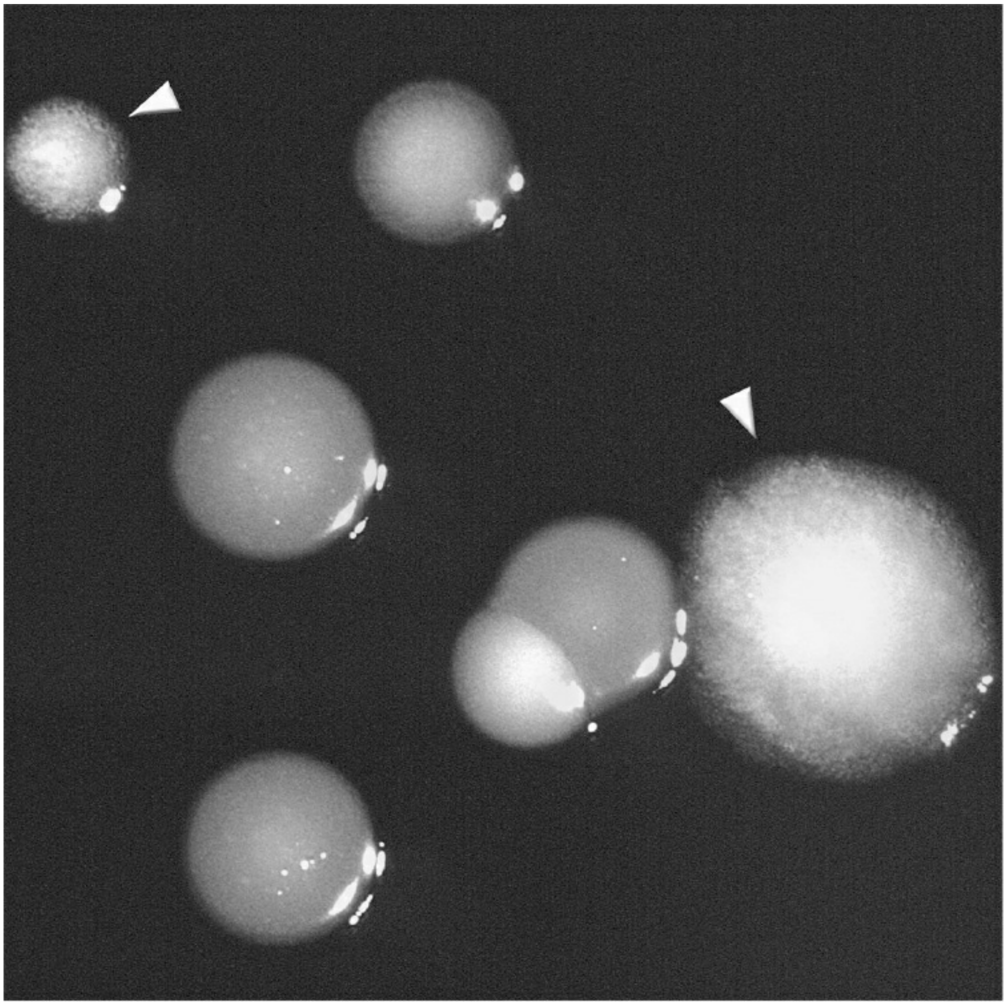


FIGURE 20.4 Two *Legionella pneumophila* bacterial colonies (arrowheads), among other bacterial colonies grown on buffered charcoal yeast extract agar. (*Courtesy of CDC Public Health Image Library*.)

Legionella continue to be studied; therefore, it is likely that more species will be identified. Each *Legionella* species may be divided into different serotypes or serogroups based on the tests used to identify the bacteria. Bacteria belonging to the same serogroup exhibit a similar response to a set of antigens used in an antibody tests. *Legionella pneumophila* serogroup 1 is the organism associated with most outbreaks of Legionnaires' disease.

Species other than *Legionella pneumophila* also cause respiratory infections similar to Legionnaires' disease. The WHO estimates that approximately 70% of *Legionella* infections are caused by *Legionella pneumophila* serogroup 1, about 20 to 30% are caused by other serogroups, and 5 to 10% are caused by non-pneumophila species. The 5 to 0% of non-pneumophila infections are based on exposure to several species, such as *Legionella micdadei*, *Legionella bozemanii*, *Legionella dumoffii*, and *Legionella longbeachae* (Bartram, et al.). In cases in Australia, the United States, and Japan, *Legionella longbeachae* has been associated with exposure to potting composts. How infection from potting compost occurs is not fully understood (Fields, et al.).

Occurrence

Legionella bacteria can be found in a wide variety of natural waters. It has been found in well water, surface water (rivers and lakes), mud, and soil samples. Even chlorinated drinking water has been found to contain the bacteria on occasion. *Legionella* are generally warm-water bacteria, and the optimum pH range for growth of *Legionella* in water is 5.5 to 8.5. These conditions are often within the range of natural and many human-made water systems.

Conditions for Growth and Proliferation

Legionella survive and grow best under specific conditions in water systems, including warm water temperature in combination with stagnant conditions, deposits, and biofilms. Stagnant conditions or water age can reduce biocide residual, reduce exposure of the organisms to the biocide, and promote deposit formation. These conditions allow complex biofilms to form and protozoa to grow.

Water Temperature

Warm water temperature is an important factor for growth of *Legionella* bacteria. Growth and multiplication of *Legionella* can occur when the water is 20 to 50°C (68–122°F). Optimal growth occurs when the temperature range is 35 to 45°C (95–113°F). They seldom grow below 20°C (68°F) and do not survive above 60°C (140°F). They may be dormant in low-temperature water but begin to grow when the water temperature rises above 20°C (68°F). Water temperature above 60°C (140°F) can kill the bacteria, if the temperature is maintained for sufficient time in contact with the bacteria (Fig. 20.5).

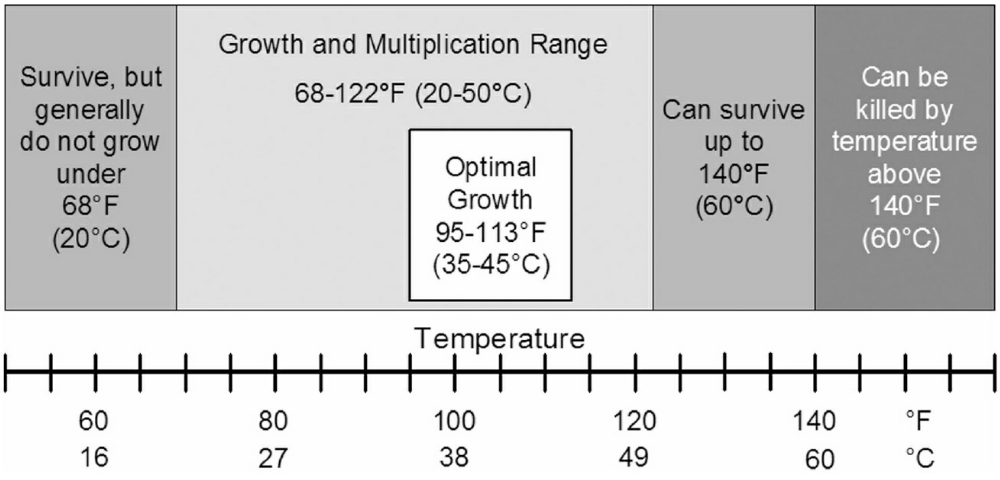


FIGURE 20.5 Illustration of the viable temperature range of *Legionella*. Sufficient contact time at temperature above 60°C (140°F) is necessary to kill the bacteria.

Stagnant Water

System design conditions that produce stagnant water or water age can promote growth of microorganisms, since microbial control programs have reduced effectiveness in stagnant areas. Stagnant water is a health concern, if the system water is contaminated with *Legionella* bacteria. Examples include non-flowing or low-flow areas in a cooling tower basin, a water tank with low flow, or dead leg piping. These areas allow sediment, sludge, scale, iron deposits to collect and biofilms to grow. These deposits can provide a safe place for *Legionella* bacteria to grow by providing a source of inorganic and organic nutrients for bacterial growth.

However, stagnation is not the primary factor that determines if biofilm will form. Biofilms also form on surfaces with high water flow rates, such as heat exchanger tubes. Flow rate may determine the type of biofilm formation (morphology and composition). *Legionella* are aerobic bacteria; therefore, the water must contain some oxygen for these bacteria to grow. Anaerobic stagnant areas of a system may be less prone to *Legionella* growth compared to other areas that have reasonable flow rates and oxygen content (such as tower fill).

Role of Biofilms

The presence of other microbial growth, including algae or bacterial biofilms, can provide a suitable environment for growth of *Legionella* (Fields, et al.). Biofilm formation is a normal part of the life cycle of many microorganisms and occurs in both natural and human-made water systems. A biofilm is a matrix of mixed bacterial populations that adhere to each other and to solid surfaces in water. Biofilms are complex heterogeneous microbial ecosystems that may consist of many bacteria, algae, and protozoa. Generally, biofilms form on submerged surfaces in a body of water, whether natural or human-made. Biofilms can form in flowing water, in areas of low water flow, and where water is stagnant. On surfaces of human-made water systems, biofilms contain a large majority of the microbial population in the system, and only a small part of the population is floating in the bulk water. Chapter 17 on Cooling Water Biology provides more information on bacterial growth and biofilms.

Biofilms provide a habitat that allows proliferation of a wide range of microorganisms, including *Legionella*. The biofilm facilitates nutrient and gaseous exchange, and protects microorganisms not only from biocides, but also from periodic changes in physical conditions like temperature (Bartram, et al.). A biofilm can protect some of the bacterial population from biocides and attempts at physical removal, especially in areas where surfaces are scaled or corroded. The availability of complex nutrients within biofilms, has led some researchers to propose that biofilms may support the survival and multiplication of *Legionella*. In an experimental study of an ideal system, a biofilm composed of naturally occurring waterborne microorganisms, has been shown to support growth of *Legionella* within that biofilm (Rogers, et al.).

Role of Protozoa

Legionella can live inside specific amoebae and some protozoa as facultative parasites. Facultative organisms are those that are able to grow in different environmental conditions, for example, in either the presence or absence of oxygen. *Legionella* are able to infest at least 14 different species of protozoa, where *Legionella* can thrive and multiply. An example of *Legionella* growth inside of protozoa is shown in Fig. 20.6. Protozoa are important for the survival and growth of *Legionella* in both natural and human-made environments. Protozoa have been detected in systems implicated as sources of legionellosis (Kwaik, et al.).

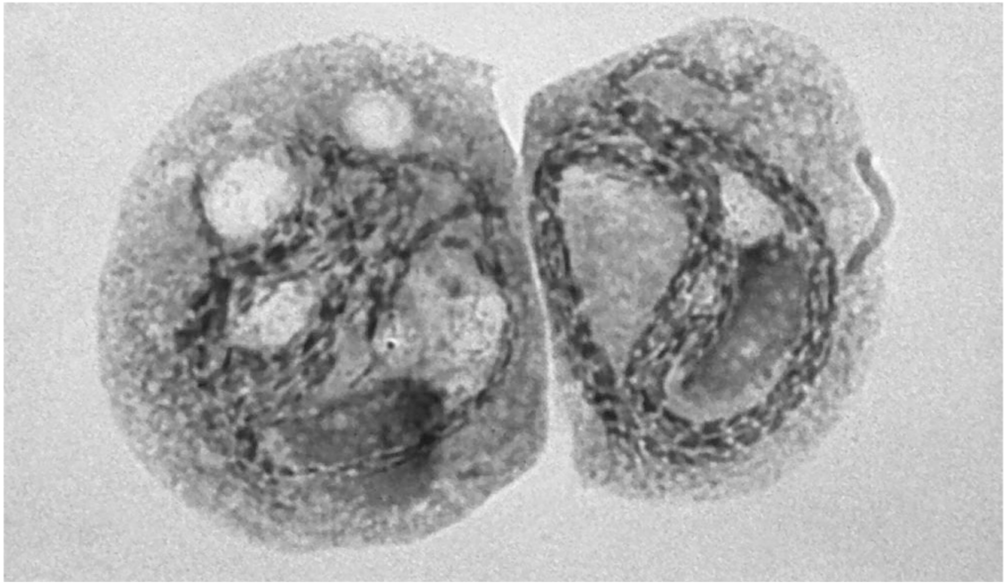


FIGURE 20.6 Two protozoa containing chains of intracellular *Legionella pneumophila* bacteria that are undergoing multiplication. (*Courtesy of Don Howard, CDC Public Health Image Library*.)

However, not all protozoa are acceptable hosts for *Legionella* growth, indicating that a degree of host specificity may be involved. Only protozoa that are capable of ingesting the bacteria and forming a vacuole (like a cyst) around the bacteria will promote growth of *Legionella*. The bacteria will multiply inside the protozoa until the bacteria rupture the protozoa cell wall and are released into the surrounding water (Fig. 20.7).

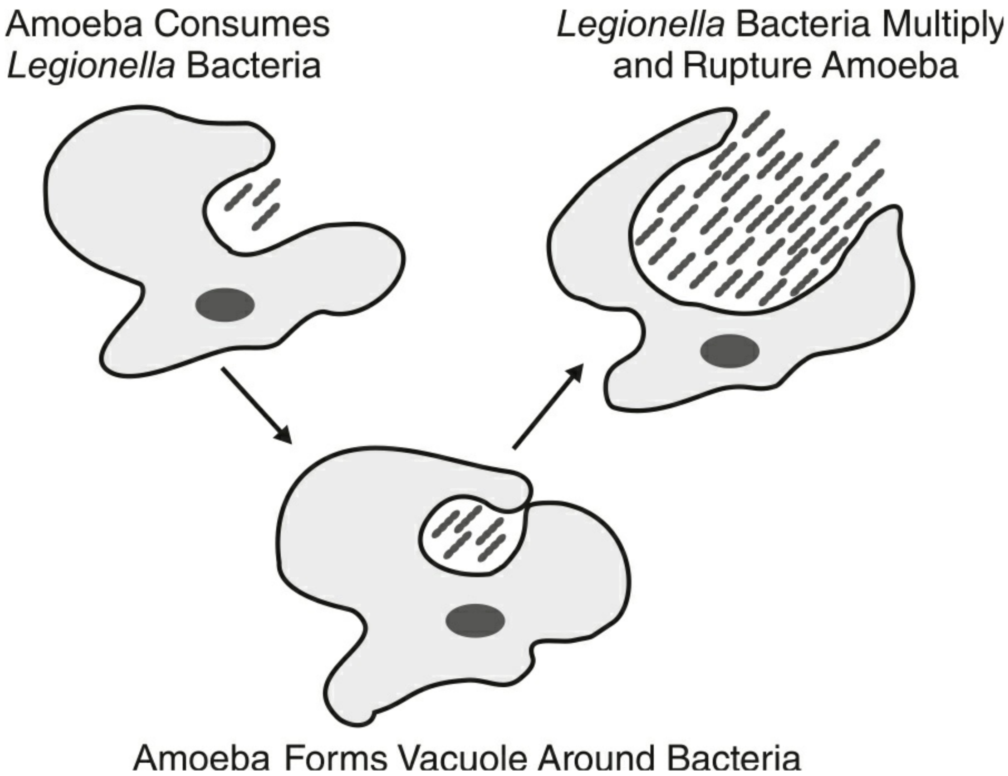


FIGURE 20.7 Illustration of growth and multiplication of *Legionella* bacteria inside protozoa.

Protozoa can help to protect *Legionella* from the effects of biocides and thermal disinfection. The presence of protozoa in a human-made water system indicates greater microbial diversity and suggests poor control of biological contamination. Under adverse conditions, certain protozoa species can form a cyst that allows them to survive through the unfavorable conditions. *Legionella* can also survive inside the cysts formed by protozoa when environmental conditions are harsh. The presence of *Legionella* within protozoan cysts can make control of *Legionella* more difficult in heavily contaminated water systems. Some researchers propose, that this mechanism, may allow *Legionella* to survive within airborne aerosols. It is now believed that adaptation to live within protozoa is what gives *Legionella* the ability to infect humans.

Operating conditions that are favorable for *Legionella* growth in a particular system may be impossible to change. However, design factors that produce stagnant conditions or allow collection of deposits may possibly be changed. Treatment to minimize biological growth in general can also help to minimize the risk from *Legionella*. See Chap. 21 on Water Management Programs for Engineered Water Systems for more details on control methods for *Legionella*.

Sources of Risk

If the water contains *Legionella* bacteria, human-made water systems that produce aerosols, mists, or sprays of fine water droplets that can be inhaled and penetrate deep into the lungs, pose the greatest risk for infection. Many different types of water systems can form aerosols and give *Legionella* the opportunity for growth. Cooling towers and evaporative condensers may be the most notorious systems, but are not the only source of legionellosis infections. Many other systems have the right characteristics and have been associated with Legionnaires' disease. Examples include:

- Whirlpool spas that aerate or rapidly agitate the water
- Hot and cold potable water systems with showerheads or other sprayers
- Spray ponds
- Humidifiers and misters
- Ornamental fountains and water features
- Supermarket vegetable misters
- Respiratory therapy equipment involving water or oxygen humidifier reservoirs
- Dental hygiene equipment water systems
- Eating ice chips (by aspiration) from contaminated ice machines

Therefore, even systems with potable water may be a source of potential infection, if the correct conditions exist and a susceptible person is nearby.

A person is not likely to get legionellosis by simply drinking water containing the bacterium, or swimming in water containing *Legionella*. The person would have to aspirate some of the water deep into the lungs for the disease to occur. Aspiration can occur when taking a breath while swimming or through improper swallowing that causes water to be drawn into the lungs. Aspiration is a documented route of infection for *Legionella* entry (Fields, et al.).

The disease is only contracted via the respiratory route, either by inhalation of contaminated aerosols or aspiration of contaminated water. Both the CDC and WHO state there is no significant evidence of transmission of either Legionnaires' disease or Pontiac fever from person-to-person contact, although one case is being investigated following to outbreak in Portugal in 2014.

Risk of Disease

The minimum concentration of bacteria in the water that causes infection is not known. A person will be infected only if the right set of conditions exists. However, the exact conditions under which an infection will occur are unclear. For example, if too few *Legionella* are present in an aerosol particle, if there are insufficient numbers of *Legionella*-containing aerosol droplets, or if the type of *Legionella* in the particle is not capable of causing disease (not virulent), then legionellosis infection of a susceptible person may not result.

The following three risk factors as illustrated in Fig. 20.8 must exist for Legionnaires' disease to be contracted by an individual:

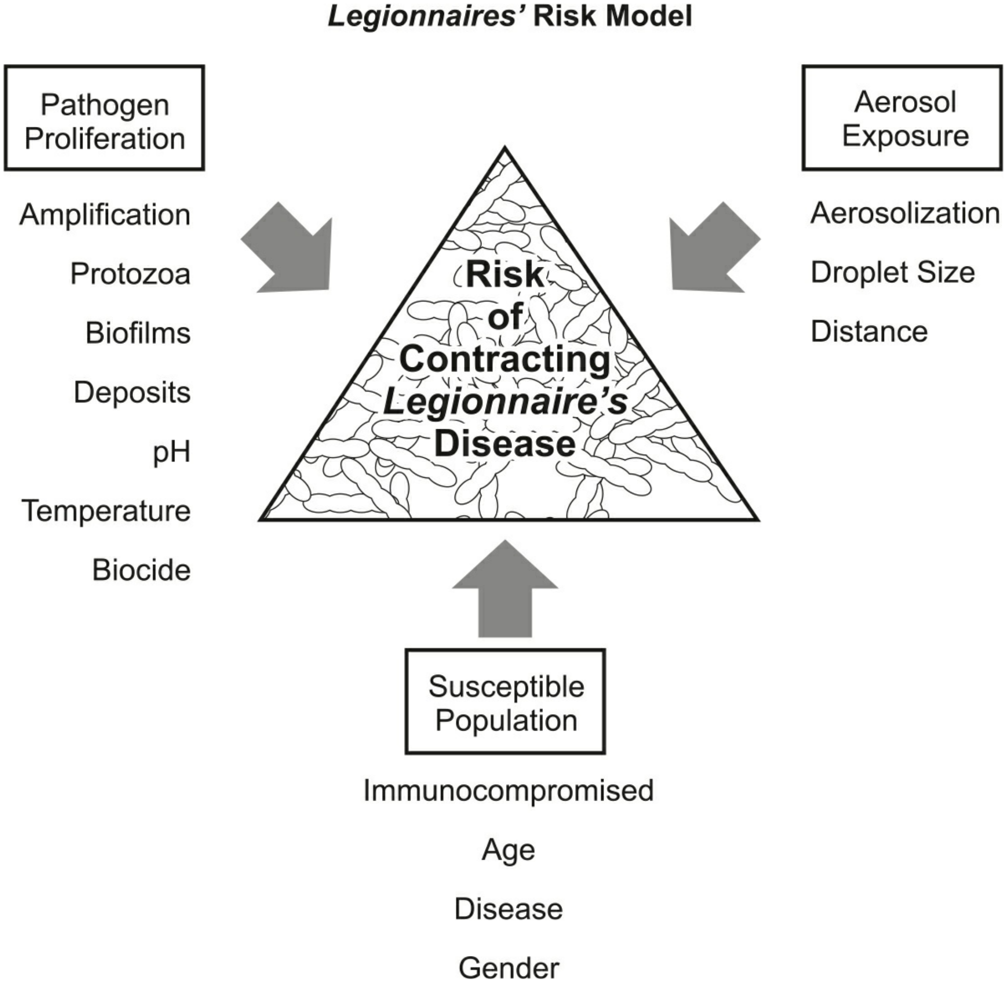


FIGURE 20.8 Illustration of the three risk factors that must combine in order for Legionnaires' disease to occur in an individual.

1. Favorable conditions for growth and multiplication (amplification) of the organism. Warm, oxygenated water, within 20 to 50°C (68–122°F), and the presence of deposits containing rust (iron), scale, or other microorganisms.
2. An aerosol of fine water droplets containing *Legionella* must be formed and aspiration of contaminated water must occur. The only exposure route for *Legionella* is inhalation or aspiration of water droplets containing the organism.
3. The aerosol or water droplets containing the infectious *Legionella* cells must enter the lung of a susceptible individual. Populations most at risk for Legionnaires' disease include, but are not limited to, the elderly, individuals with suppressed immune system, and individuals

> with pulmonary or liver dysfunction. However, even people with no previously indicated health risks have contracted Legionnaires' disease.

Therefore, determining whether a specific water system could cause an outbreak of legionellosis requires an assessment of risk, and is not a simple "yes" or "no" answer. The disease may not result when someone is merely exposed to water containing *Legionella* because the other risk factors are absent. Similarly, the presence or absence of *Legionella* bacteria in a water sample is not a measure of risk. *Legionella* may be present in a water system but not detected in the tested sample of water for a variety of reasons. Chapter 21 on Water Management Programs for Engineered Water Systems covers the aspects of detection, risk management, and water treatment protocols in more depth.

CHAPTER 21

Water Management Programs for Engineered Water Systems

Engineered or building water systems such as centralized cold and hot potable building water systems and nonpotable building water systems can become colonized with *Legionella* and other opportunistic waterborne pathogens and can present a significant risk to infection in human-occupied buildings. At-risk buildings can include commercial, institutional, multi-unit-residential, and industrial buildings, including, but not limited to, hotels, office buildings, hospitals, and other health care facilities, assisted living facilities, schools, universities, commercial buildings, industrial buildings, and centralized systems in multifamily residential buildings. Buildings with noncentralized building water systems and single-family residential buildings can also be at risk.

Traditionally, the water treatment industry has reviewed operation of engineered water systems purely from the perspective of plant efficiency or an operational performance goal. Consideration has focused on reducing potential for scale formation, minimizing corrosion, and preventing microbiological proliferation. Poor control of these parameters causes loss of system efficiency and increased operational costs. These elements are still key performance indicators, but as identified in previous chapters, there is an increasing concern on a global scale over waterborne disease associated with *Legionella* and other waterborne pathogens that may reside within an engineered water system. Now, in addition to traditional water treatment considerations for cooling systems or the general operation and maintenance of potable water systems, the owner of the legal responsibility for the site is required to manage exposure risk of workers and members of the public to such organisms. In some countries, the need for this consideration is a statutory requirement. In the absence of such regulatory enforcement, control of *Legionella* is still deemed a "duty of care" responsibility.

With respect to maintaining hygiene and reducing risk within the engineered water system, a sound knowledge of the ecology of the microorganism in question is required, along with expertise to translate this knowledge into good working practice. This requires a special skill set to those employed for traditional operational management of engineered water systems and necessitates an understanding of water safety to be able to (1) assess the risks, (2) determine the best strategy to reduce risk, and (3) understand the requirements for proactively managing risk to a health-based goal within the context of a written Water Management Program, Water Safety Plan or Risk Assessment (collectively, the "*Program*").

Acknowledging the fact that the number of cases of legionellosis has historically been under-recognized, under-diagnosed, and under-reported, the actual number of people diagnosed with Legionnaires' disease has increased significantly over the years and outbreaks have occurred in many geographical regions of the world. This may be attributed to a number of factors such as differences between surveillance systems used in individual countries and aging population and infrastructure. In order to align surveillance methodology and monitor cases of legionellosis, many countries within Europe have contributed to an international surveillance program (European Legionnaires' disease Surveillance Network—Eldsnet). In the United States, outbreaks are typically reported by local state or city health agencies to the Centers for Disease Control and Prevention (CDC).

Collated results from global surveillance data indicate outbreaks of legionellosis have been associated with several different types of systems, including cooling systems and hot and cold potable water services such as those provided within buildings. In response to worldwide concern over water safety and implications of creating risk to health, various management programs have been specifically designed to assist the owner of engineered water systems, to reduce the risk of exposure to *Legionella*, and meet regulatory requirements of countries in which they operate. Although it can be concluded that the terminology may differ within some of the control programs used globally, there are basic components of risk management and keeping the water systems safe that are common to all processes.

For example, it is recognized that a nominated manager who may lead a team (water safety group or program team) would be overall responsible for identifying any water containing systems where *Legionella* may be present, and where operation of those systems may create an aerosol, which could be inhaled. The manager (with assistance from colleagues) is then required to prepare a risk statement and provide a suitable *Program* to control risk. Working knowledge of such systems and implementation of specific water safety programs is an important management strategy for reducing risk of exposure to these bacteria. This is in accordance with both legislative and good practice standards requirements of many countries and is deemed best practice.

This chapter has been compiled in order to provide an understanding of the manager's role to comply with global legislative and best practice requirements to control and limit exposure to *Legionella* bacterium (and by default other opportunistic pathogens) that may be associated with engineered water systems.

Managing the Risk: Regulatory Position and Global Guidance

Sporadic outbreaks of legionellosis continue to occur. One typical response to such an event at a national level may be to review and possibly revise current statutory guidance. In some countries, general health and safety regulations may not specifically mention *Legionella*, but may have generalized references to the protection of personnel within the working environment from biological agents or environmental hazards. Fortunately, several countries have realized that exposure to *Legionella* is preventable, but only if health-related risks are assessed and preventative practices are implemented and monitored.

As a consequence, several countries have introduced regulatory instruments, which require senior management or those responsible, for an industrial plant, large commercial buildings, hospitals, or managing government owned buildings, which may be frequented by the general public or employees, to consider whether there is a foreseeable risk of exposure to *Legionella*, and whether sufficient emphasis has been placed on reducing that risk.

Such guidance now exists and is practiced in many countries, for example, the United Kingdom, France, the Netherlands, Australia, Spain, Germany, and Italy. In the United States, the American Society of Heating, Refrigerating and

Air-Conditioning Engineers (ASHRAE) produced ANSI/ASHRAE Standard 188 entitled “Legionellosis: Risk Management for Building Water Standards,” as a practice standard for managing risk, which is gaining acceptance and has been codified by the state of New York and the city of New York as a requirement for managing risk in cooling water systems. In the event of an outbreak of legionellosis or failure to satisfy local government inspection, senior management responsible for control procedures will likely be investigated, in order to determine whether there has been a breach of any legal duty, with the threat of financial or imprisonment penalties as a consequence of a work-related death associated with their premises. In the United States, the Occupational Safety and Health Administration (OSHA) has authority under the General Duty clause, to issue fines and citations if facilities are found to be negligent. From an international perspective, the World Health Organization (WHO) has recognized the concern of possible exposure to *Legionella*, and in 2008 released a publication entitled “*Legionella* and the Prevention of Legionellosis,” which reviews general epidemiological aspects and approaches to risk management. In 2011, the WHO also released documentation relating to water safety in buildings.

All this available information can be used by individual or corporate organizations, to prepare a site-specific *Program*. In general, similar recommendations are identified within all previously mentioned guidance, and a *Program* may be generalized into the following process (Fig. 21.1):

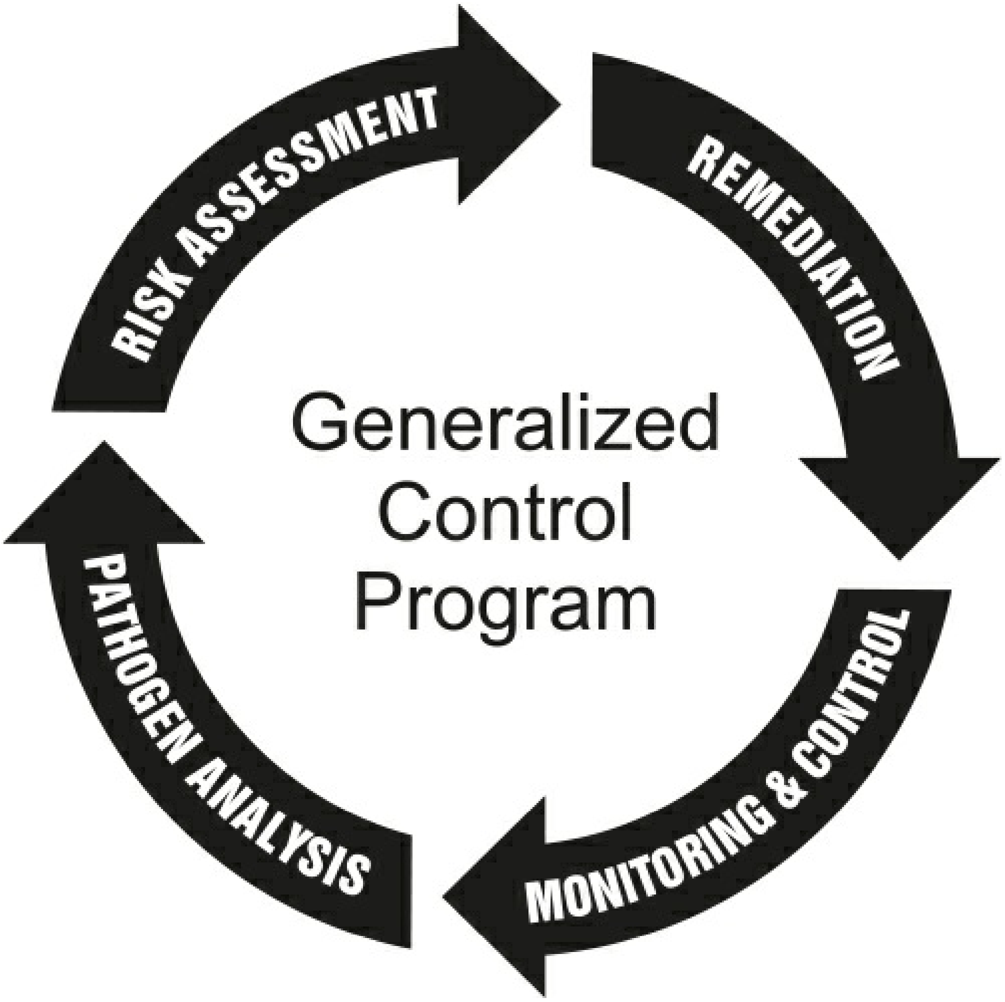


FIGURE 21.1 Elements of a water management program.

1. Establish a *Program team* who owns the responsibility for the development, implementation and management of the *Program*. The team should appoint a responsible person or duty holder.
2. Describe *building water systems* with text and simple flow diagrams or schematics.
3. Assess *building water systems* to determine where *Legionella* could grow, where sources of aerosols can occur and the risk of human exposure. Goal is to assess and prioritize risk.
4. Define where *control measures* should be applied (plus applicable control limits) and how to monitor them. Goal is to identify needs for safe operation including system maintenance, regular examination or inspection, and system testing and monitoring.

5. Establish procedures for *corrective action* when control limits are not met. This includes provisions for instruction and training plus escalation and incident response plans.
6. Confirm the *Program* is working as designed and it is effective on a regular basis (i.e., quarterly). Goal is to validate the *Program* when implemented as designed, effectively control the hazardous conditions throughout the building water systems, and the goal is to verify the *Program* is being implemented as designed.
7. Document and communicate all activities.

General Management Considerations

Failing to employ preventative control programs can carry severe consequences such as sickness and fatalities that can be associated with an outbreak of legionellosis. Numerous financial penalties can affect the incumbent company, for example, adverse media exposure, share price fall, or brand damage. In some countries, a charge of breach of health and safety guidance may reside on government websites that are open to the public domain. Business associates, both future and present, may view this information.

The information provided below identifies the need to introduce various management processes and discusses the requirement to determine individual responsibilities of all personnel involved with a *Program*.

Generally, health and safety responsibilities for an individual site cannot be transferred to third parties, such as companies offering services to assist compliance. However, service company personnel may be invited to participate on the *Program team*. It is important, therefore, that the responsible manager ensures that the services provided actually satisfy the need of the site, and that they form an effective part of the *Program*. It is equally important that clear lines of responsibility and communication are identified between the client and service provider. It is acknowledged that inadequate management, lack of training, and poor communication have all been associated with outbreaks of Legionnaires' disease, which emphasizes on the importance of effective management of the *Program*. Such comments are borne from the experience of previous outbreaks, where the consequences of mismanagement have resulted in personal injury or death, and have become critical key learning points.

It is vitally important that all individuals involved in the risk management process, which includes company senior management or owners, engineers, health and safety representatives, and associated service providers, understand their individual roles and responsibilities in relation to reducing the risk of exposure to the *Legionella* bacterium. Ideally, right from the start of any contractual agreement, it should be defined by individual, who will do what, where and when. Training will need to be undertaken to correspond to the level of responsibility accepted.

Assessment of Risk

The most logical starting point when considering a *Program* is to determine whether an inherent risk actually exists in relation to the specific hazard being considered. In most global *Legionella* control guidelines, the initial phases of a control program involve undertaking assessment of whether a risk actually prevails and where it is reasonably likely to occur. Use of such terminology as risk assessment may differ from one guidance to another, but there is generalized acceptance of establishing a baseline of risk that is common to many health and safety practices.

The complexity of assessing risk has in some instances, led facility owners and managers to delay establishing a *Program*. However, practical experience and observation suggest that prioritizing risk assessment and developing a site specific *Program* to mitigate the risk of legionellosis is both prudent and justified. Since facility managers hold great responsibility and play a number of different roles, they cannot be expected to be experts in all areas. For specialized assessments such as *Legionella*, it is not unusual for companies to utilize external service providers to provide competent trained risk assessors or subject matter experts. Alternatively, a person or nominated team with detailed understanding of the system and risk factors, must undertake the assessment to characterize the risk.

Health and safety professionals recognize the risk assessment process, as a natural beginning to laying a foundation for the ongoing *Program*. Assessment requires being “suitable and sufficient;” in other words, it should consider all aspects of *Legionella* control and how mechanical, operational, and control procedures all interrelate. Since this bacterium has been isolated from drinking water in low numbers, even systems utilizing potable water need to be assessed. Consequently, cooling systems, whirlpool spas, hot and cold potable water systems, ornamental fountains and water features and other water systems that have the potential to release contaminated water mists have all been identified as "at risk" systems. Sites previously described earlier that contain such water systems or utilities have all been identified as sources of outbreaks, which when analyzed retrospectively, could have been prevented. Most global *Legionella* guidance views legionellosis as a preventable disease.

In relation to content, the risk assessment should be sufficiently detailed to identify and assess risk of legionellosis from all work activities and water sources on site, and to describe necessary precautionary measures needed. Each system assessment should include a process to identify and evaluate potential sources of risk, particular means by which exposure to *Legionella* bacteria is to be prevented, and means by which risk from exposure to *Legionella* bacteria is to be controlled, if prevention is not reasonably practicable. Such studies should consider all mechanical, operational, and management aspects and how these factors can be interrelated to decrease risk potential. As mentioned, if the risk assessment identifies significant risk that cannot be eliminated, the responsible manager should implement an appropriate control scheme.

A *Program* is developed using a standardized model to identify potential hazards and control measures. Risk of legionellosis is a function of many factors that can be grouped into three categories:

1. Growth Risk—the likelihood of microbial growth in the water system
2. Aerosol Risk—the likelihood of the release of aerosols or water mists from the water system
3. Human Risk—the likelihood of having susceptible people present who may come in contact with contaminated water mists

The risk of harm is a function of these factors that combine to form the causative chain, which in severe cases, can lead to infection. Each category is further discussed within the context of assessing risk potential that may be associated with an engineered water system.

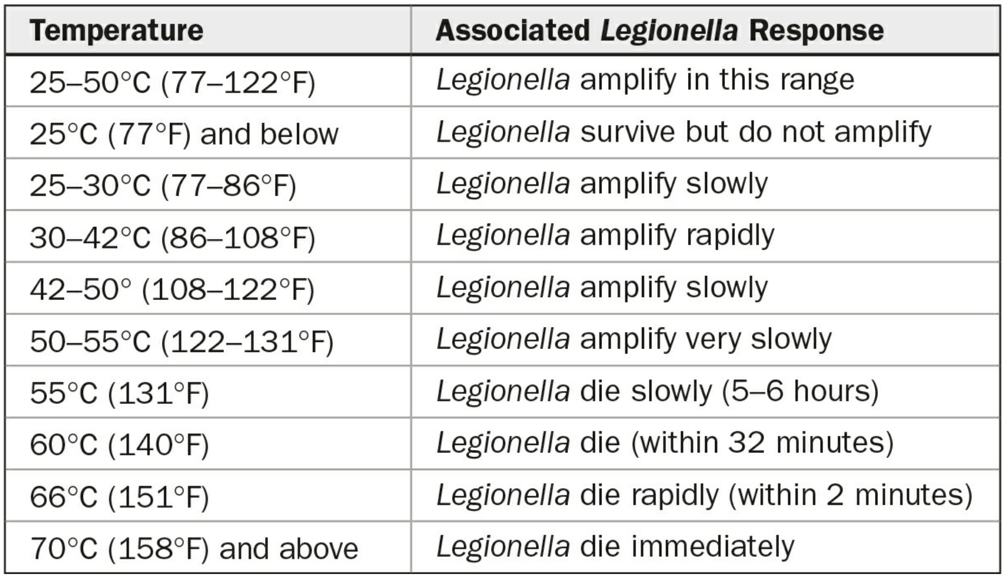
Growth Risk

With respect to proliferation potential, the following need to be considered on each individual part of a system:

- Water temperature
- Deposits
- Presence of other organisms
- Low-flow areas

Water Temperature

Temperature is an important factor in keeping the *Legionella* bacterium active, since as temperature increases the normal biochemical reactions inside the cell also increase. This bacterium has an ideal growth temperature of about 37°C (99°F), but temperatures in the range of 25 to 42°C (77–108°F) can provide an ideal growth environment for *Legionella*. The general growth range is 20 to 50°C (68–122°F). When considering different water systems, the ideal situation would be to avoid temperatures in the growth range (see Table 21.1); the reasoning to keep hot water hot and cold water cold. If a cooling system is present, using temperature to control growth is not a feasible option, and additional control strategies are needed.



Temperature	**Associated *Legionella* Response**
25–50°C (77–122°F)	*Legionella* amplify in this range
25°C (77°F) and below	*Legionella* survive but do not amplify
25–30°C (77–86°F)	*Legionella* amplify slowly
30–42°C (86–108°F)	*Legionella* amplify rapidly
42–50° (108–122°F)	*Legionella* amplify slowly
50–55°C (122–131°F)	*Legionella* amplify very slowly
55°C (131°F)	*Legionella* die slowly (5–6 hours)
60°C (140°F)	*Legionella* die (within 32 minutes)
66°C (151°F)	*Legionella* die rapidly (within 2 minutes)
70°C (158°F) and above	*Legionella* die immediately

TABLE 21.1 Temperature Effects on Survival and Amplification of Laboratory Strains of *Legionella* (US-CDC)

Hot water should be stored at 60°C (140°F), and hot water should be at or above 124°F (51°C) everywhere throughout the system to the point-of-use. In addition, the hot water return from the point-of-use should be consistently above 122°F (50°C), unless other, compensating control measures are used. Appropriate scald controls may be necessary to achieve the desired hot water temperature.

Cold water should be stored at less than 20°C (68°F), and in general, cold water should be distributed and delivered at temperature below 25°C (77°F), if practical. (Note: lower temperatures may be required by some guidance documents) If cold water temperature exceed 25°C (77°F) in any part of the system, there is greater potential for amplification of *Legionella*. At water temperature above 30°C (86°F) the potential for amplification of *Legionella* increases significantly. When water supplied to the building is near or above 25°C (77°F) and when environmental conditions, building water system design or operating conditions result in cold water temperature above 25°C (77°F) in any part of the system, other physical or chemical control measures should be considered for *Legionella* control.

Deposits

The presence of sediment, sludge, scale, and corrosion product has been identified as a source of inorganic and organic nutrients. In general, systems should be kept as clean as possible. This does not just apply to cooling towers. General cleanliness of the system is a paramount control factor in all systems and in particular for those containing large amounts of piping, which provides a large surface area. Microbiological activity can potentially migrate to such surfaces. In a similar way, the bathing load of whirlpool spas should identify the frequency for thorough cleaning to reduce risk to bathers.

Presence of Other Organisms

Legionella are often found within more dynamic environments associated with biofilms and higher life forms (amoeba). Biofilm generation is a normal part of the life cycle of most microorganisms. A biofilm is defined as a matrix of bacterial populations that are adherent to each other and to surfaces or interfaces. Biofilm provides a habitat that allows proliferation of a wide range of microorganisms, including *Legionella* although *Legionella* does not form biofilm, but rather is a “squatter” within biofilm where there is a favorable growth environment. In engineered water systems, over 90% of the microbial population is present on surfaces and in aggregates, not in bulk water (Figs. 21.2 and 21.3). Since *Legionella* are thought to be vulnerable organisms, they prefer to hide out and proliferate within biofilms, where they are protected and can even gain nutritional advantage.

FIGURE 21.2 Biofilm in tower fill.

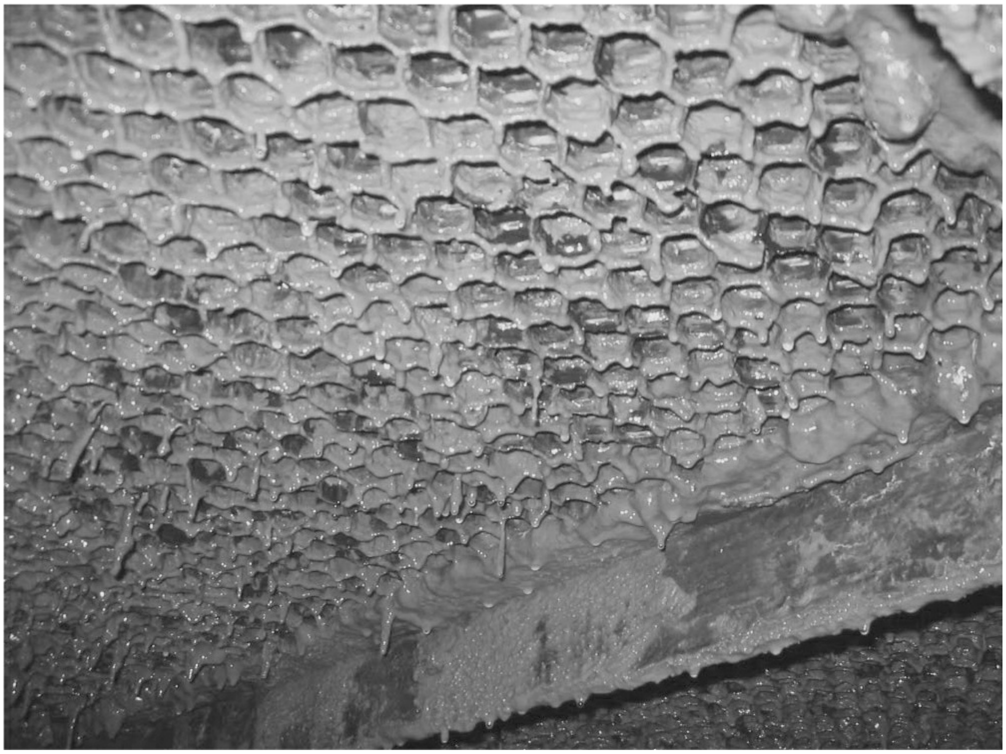


FIGURE 21.3 Severe biofilm on the underside of tower fill.

Amoebae have been isolated from various water systems. These organisms can become infected with *Legionella*, suggesting that amoebae are a reservoir for these bacteria.

These biological principles obviously enable the organism to survive and reproduce, and this level of contamination may be directly linked to available food source or absence of suitable control factors. Therefore, unexpected or even predictable contamination of a cooling system with process materials (hydrocarbons, sugars, etc.), may provide ideal growth conditions at normal operating temperature. Such contamination may overwhelm the current treatment program, making it ineffective and rendering the system vulnerable. Maintaining cleanliness in water systems is of paramount importance for controlling microbiological activity.

Low-Flow Areas

Water stagnation or water age encourages biological growth and has been implicated as a source of contamination in previous outbreaks of legionellosis. Dead legs and slow water turnover areas are prone to supporting growth. Such areas may include:

- Low flow zones of heat exchangers, where temperature and buildup of deposits particularly favor proliferation of microorganisms
- Blocked areas of cooling tower fill, where no biocidal treatment might penetrate
- Water tanks serving domestic systems that have a low water turnover rate

Piping containing water that is exposed to heat gain may be considered a dead leg area. Buildings or factories that are fed directly by water mains and do not have tanked water storage systems can create a risk. In some cases, the control program involves flushing of these little used or low-flow areas.

Aerosol Risk

Since legionellosis is contracted through inhalation of a contaminated aerosol (water mists), any engineered system that might create an aerosol (Figs. 21.4 and 21.5) as part of its operation needs to be considered in relation to risk potential. Should an aerosol be produced by a system that is operating at a temperature to allow *Legionella* proliferation, and where conditions provide support via nutrients, pH, and questionable cleanliness, such a system may be breaching health and safety guidance in several countries. More importantly, such a system may provide a source of *Legionella* that might infect the final link in this causative chain—the susceptible individual.

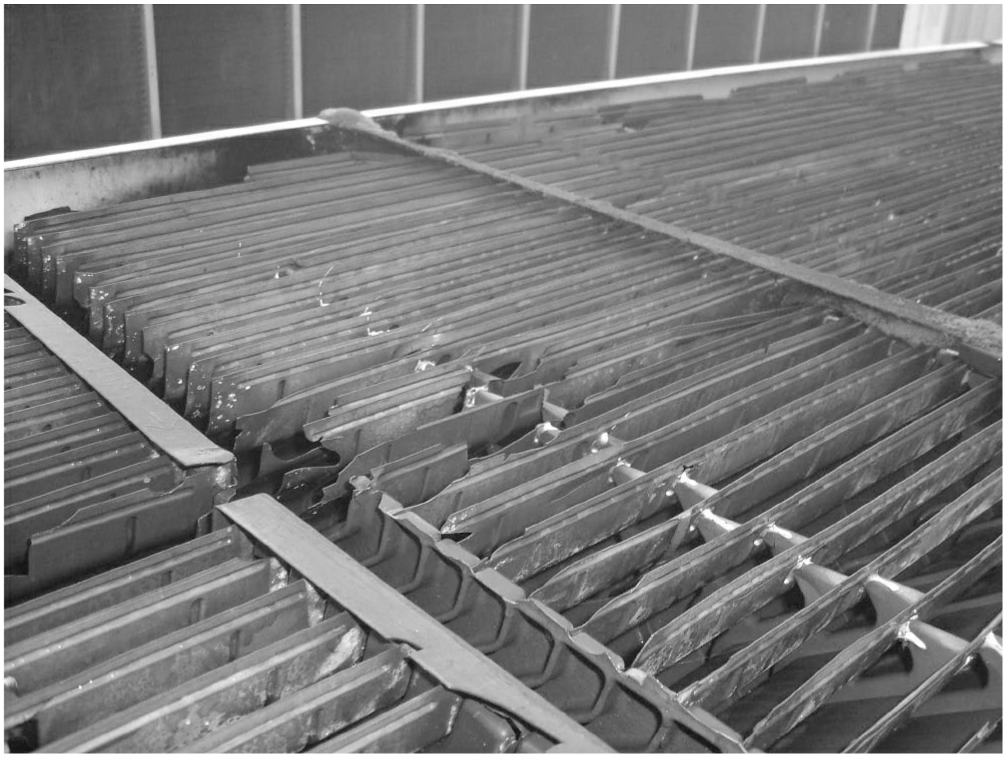


FIGURE 21.4 Damaged drift eliminators are a potential problem for aerosol release.

FIGURE 21.5 Poor control of aerosol release from a cooling tower.

Risk assessment should identify sources of risk and suggest remedial action for implementation as part of a corrective action plan. Underlying all the mechanical, operational, and chemical aspects of the control plan is still management of the process. Without proactive management to ensure the control plan is implemented and maintained, even the best risk assessment available is likely to fail.

Human Risk

It is generally accepted that certain individuals are more susceptible to legionellosis than others. Individuals likely to be infected are males, generally over 40 to 65 years old (varies depending on the reference), or those with underlying disease like diabetes, heart disease, or those on immunosuppressant drugs. Heavy smokers and those suffering alcohol abuse are also deemed susceptible.

Manage the Risk: Water Management Program

A site specific *Program* (aka, control programs, control scheme, and water safety plans) is necessary to manage risk. It is essential to the control scheme defined in the *Program*, that any remedial work identified by the risk assessment should be implemented, and consideration given to conditions that inhibit *Legionella* proliferation and dispersion of an aerosol. It is important to note that a system risk may change during the cycle of its operation. For example, an intermittently used cooling tower may provide little risk from exposure to *Legionella*, but while offline, microbiological activity that has developed during the idle time, can seed the system once it is brought back into service. Such systems need to be cleaned and treated correctly to minimize any inherent risk. Hence, many consider intermittently used cooling towers as a major risk.

Where the risk assessment identifies a reasonably likely risk, management must initially consider whether the particular system can be removed and replaced by a lower risk system. It is considered good practice to demonstrate these considerations have been undertaken. If elimination is not practicable, it is the responsibility of the site to ensure a scheme for controlling risk from exposure, is prepared and properly implemented and managed. This scheme should include, but is not limited to:

- Up-to-date schematic diagram
- Description of correct and safe system operation
- Precautions to be taken and associated checks that ensure efficacy of the control scheme
- Remedial actions should the scheme be ineffective

Water Management Program for Cooling Systems

In the example of cooling systems, the water treatment program is a major part of the *Program* for reducing risk. This is obviously in addition to any mechanical or operational remedial actions suggested to reduce risk potential. The latter may include replacement of damaged drift eliminators, installation of aerosol reduction equipment, or even removal of outlets that are infrequently used and thereby create a possible contaminant source to the rest of the system.

Cleaning and Disinfection Programs for Cooling Systems

Failure to maintain cleanliness of the system and the water in it has been associated with several outbreaks of legionellosis. Most global guidance documentation identifies that cleaning and disinfection techniques are an important part of overall *Legionella* control strategy. Routine mechanical cleaning and disinfection of the cooling tower should be conducted in accordance with local guidance, or when the system is deemed dirty by either visual or operational factors (e.g., loss of cooling).

It is important to note that often a cursory visual inspection may give the false impression that tower packing is clean, but upon removal, deposition is often found in lower layers of the packing. Experience has shown that application of chemical cleaning procedures alone is often less effective than undertaking a chemical and manual cleaning.

The risk assessment and condition of the system dictate the specific cleaning frequency; although historically, there are periods when systems may be at higher risk. Particular care should be taken in the following situations:

- When either commissioning or decommissioning a cooling system
- In the event of major modifications to the system
- After a period of being out of service in excess of one month

- Where results indicate loss of control
- Following a suspected outbreak of legionellosis
- Where determined by local guidance for a particular industry (e.g., health care)

The method of cleaning should be selected after review of system conditions, the risk assessment, and previous history of the system. For example, in cases where heavy scaling is present, specific cleaning programs or replacement of tower fill is required. Therefore, the cleaning program may be site specific and require external expertise provided by the service provider. Best practice adopted by several countries includes addition of sodium hypochlorite (bleach) to achieve a free residual chlorine level of 5 mg/L, maintained for 5 or 6 hours (depending on local requirements) pre- and postphysical cleaning. Alternative programs, as identified in local guidance, can be implemented.

In-situ or in-place cleaning techniques may be considered if tower internals cannot be accessed. However, whichever cleaning protocol is used, it is important that the time taken to undertake such cleaning is fully scheduled into the cleaning program and that process is not compromised in any way. Incomplete cleaning and disinfection programs because of production pressures constitute a noncompliance in many countries. Supplementary control procedures such as increased monitoring or additional chemical treatments are then required.

In making a decision on the cleaning program, consideration should be given specifically to the cleanliness of the tower fill. If dirty, the fill should be removed and physically cleaned or replaced. In countries where fill removal is a legislative requirement (unless proof is available to demonstrate cleanliness), the statutory duty holder for the site must be made aware of this obligation. Techniques such as employing borescopes may be considered as additional evidence of cleanliness.

For systems that are continuously operated and cannot be shut down for cleaning, like those associated with heavy industry and large power stations, online disinfection (also known as super chlorination) should be carried out every three months or when results indicate a lack of control. This chlorination (to include addition of a dispersant) typically involves dosing the system to achieve 5 mg/L free residual oxidant for 5 or 6 hours, depending on local requirements. It is good practice to visually inspect all cooling towers if the system becomes available and if required, clean all accessible areas. In such systems, application of automated dosing and monitoring programs is often favored. Since physical cleaning is often not an option apart from periods of plant closure, the objective is to address the balance of risk by applying additional control factors. These supplementary control factors require proof of being effective, and one common approach is to increase monitoring of the system key performance indicators and to continuously apply biocide treatment.

Review of Control Measures for Cooling Systems

So how do we prove that the proactive management has been effective? Obviously monitoring the system closely helps determine whether the employed control and risk reduction procedures have achieved the objective. Monitoring programs should be devised to ensure the treatment regime and all other aspects of the control program continue to reduce risk and control can be demonstrated. When situations arise where control limits are not met, a defined management process should be followed to firstly undertake any remedial action necessary; prove that the action taken has been effective in reducing any incumbent risk; and finally ensure the event is documented. In some countries, this is called a defect/action log or escalation process. This log details all personnel held responsible for undertaking a specific action in order to return the system to a steady state and all correspondence between personnel. Such systems should be auditable, and the review process should validate and verify that the *Program* has been effective. Typical tests to include are:

- Checking system pH
- Enumeration of general bacterial levels, using for example, dip slides
- Analysis of free halogen residual
- Conductivity measurements

Such tests should be carried out on a regular basis, at least weekly or as defined by local guidance and form part of a management program. Agreement as to whether site personnel or the service provider conducts these analyses needs to be defined in the commercial contract. Free residual halogen should ideally be recorded on a daily basis, or a system to measure automatically would be deemed good practice and provide enhanced monitoring. All results must be recorded in site documentation and be available for inspection by the service company, or if the market place is legislated, by the regulating authority. Arrangements should be made for regular review meetings (recommend at least once per year minimum) in order to discuss the various control parameters, and ensure good communication by all parties concerned in the risk management. These meeting should determine the overall effectiveness of the control program.

For each of the tests above, it is important to both define the specific test methodology to use, to identify specific control parameters and to calibrate monitoring equipment at predefined intervals.

In addition to any chemical or microbiological testing, daily physical inspection of functionality of dosing equipment, cleanliness of system, chemical drum levels, etc. is considered good practice. Any comments from such a review should be recorded. Calibration of equipment should be conducted periodically in accordance with manufacturer's recommendations. Daily inspections are often the responsibility of site personnel and must be identified under designation of responsibilities within the control plan. Site personnel must therefore, be trained and competent to interpret results, take appropriate action, and communicate such details to the service provider. Accessible areas of the system should be inspected for damage or signs of contamination during daily inspections.

Arrangements should be made for dosing, testing, draining, and isolation during idle operational periods, with subsequent cleaning and disinfection. If the system is out of use for periods of longer than one week, arrangements must be made to dose the system with biocide immediately on reuse. If the cooling system is left idle for longer periods, especially during warm periods, the system should ideally be cleaned and disinfected.

Sampling and testing for the presence of *Legionella* is a useful addition to the monitoring program. Samples should be taken at least quarterly, although in some cases law may require a higher frequency. Additionally, specific conditions might arise where additional testing to those deemed routine would be important. Sampling frequency and protocol should be agreed upon between the site owner and service provider, and written into a formal service agreement, such that both parties know and understand the logic behind any intended sampling program. More frequent *Legionella* testing is required when determining efficacy of a new program or where problems have been experienced with the existing control program. If deviation from the standard control programs occurs, additional testing is required as evidence-based practice to prove that excursions in the risk management have been rectified. For example, lack of delivery of biocide due to air binding of a dosing pump increases risk potential, and additional testing may be necessary to prove continued control. Reasons for additional testing should be documented in the site file.

Heterotrophic aerobic bacteria dip slides are a simple technique for determining general bacterial activity of water samples although it is acknowledged that in certain countries use of dip slides is limited by regulations. The testing protocol for dip slides should ideally be on file such that the procedure for testing can be referenced when audited. Tests involving the use of adenosine triphosphate (ATP) may be considered to supplement the control program. Any deviation from the trend may indicate an increase in microbial activity and risk and warrants investigation. It could mean simply that a biocide product drum has emptied or that the system has suffered process contamination. In addition, for due diligence, if site personnel undertake dip slide testing, the service provider should review the testing protocol to ensure good practice.

Control Scheme for Hot and Cold Potable Water Systems

Hot and cold potable water systems in buildings can create a risk from legionellosis if poorly managed. Many individual cases of infection have been associated with such systems. Many of the control factors associated with cooling systems play a part in reducing risk from these systems. However, in most cases, water supplied to the utility is usually of potable water quality, and the level of *Legionella* contamination is expected to be at a very low level. Risk of legionellosis occurring from hot and cold potable water systems is amplified by failures in design and operation. One example being that some systems may have water feeding directly to an outlet, where others take water and store it in tanks before distribution. The use of water storage tanks may be limited by local regulations. Many health authorities implement *Legionella* control policies in recognition of them having a highly susceptible population, and that any water utility may pose risk to health. For such systems, the main risk reduction program employed by many countries is control by temperature, following a simple rule of “keep hot water hot and cold water cold.” Proof is required to ensure that this simple control process remains active. In some large sprawling distribution systems within complex buildings, attaining desired temperatures is sometimes impractical without significant capital investment. In such situations, a secondary disinfectant may be applied. Whichever control method is employed; risk assessment is still the initial starting point for a *Program*. The following points are generalized in relation to reducing microbiological activity, including *Legionella*.

System Design Factors

Distribution systems taking water from the source of entry to a building or factory, to a particular outlet, need to be installed by competent people who use only approved fittings and materials. Incorrect materials might not only contravene local standards in relation to water supply regulations, but may also provide suitable habitat for microbiological activity. In a potable water system, extensive piping and tanks (Fig. 21.6) provide a large surface area on which to deposit, and if organisms are provided with a suitable food source and temperature, biofilm formation can easily occur. Reference should be made to local standards, as certain materials have been identified as supporting microbiological growth (e.g., rubber sleeves within certain flexible fittings).

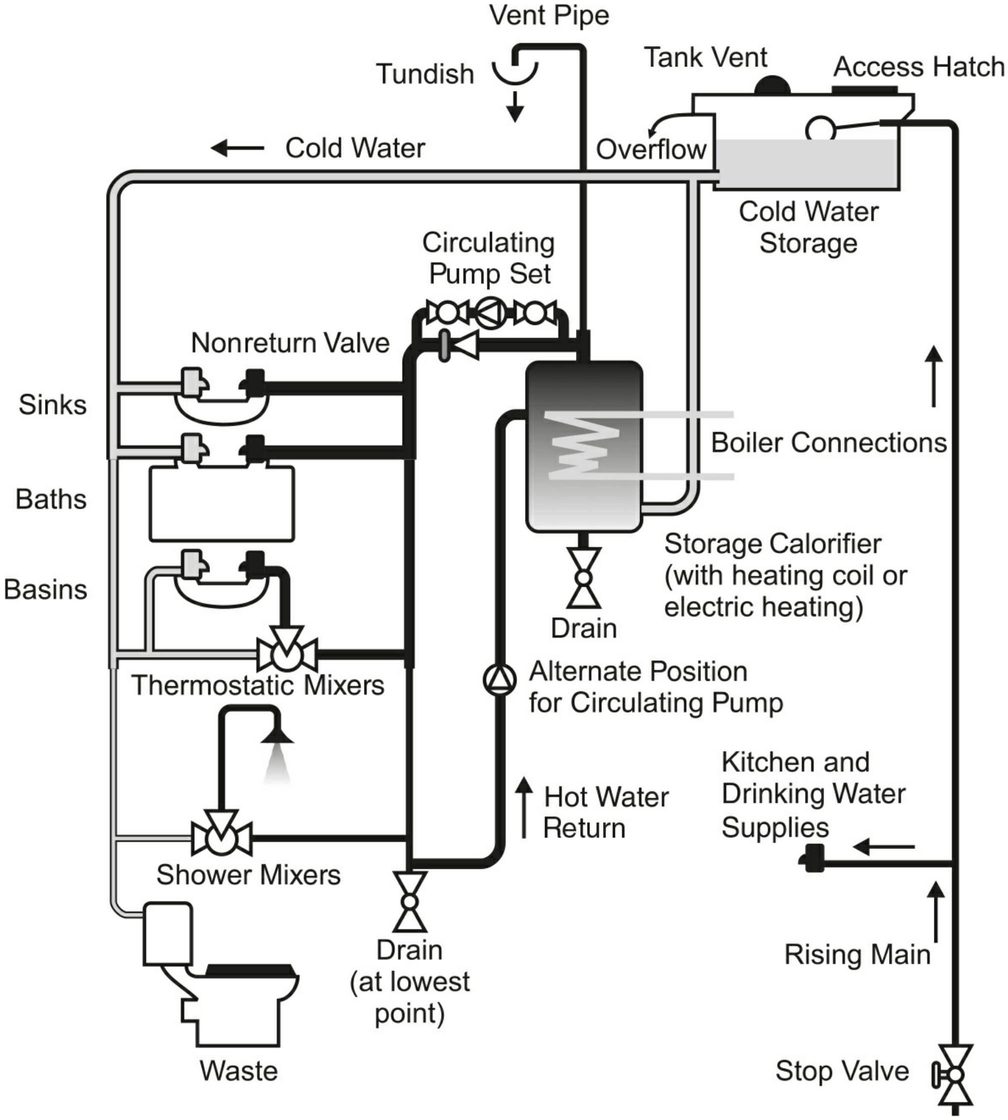


FIGURE 21.6 Example of water distribution system featuring a storage tank.

Water entering an industrial or institutional site is frequently stored in a tank, which can be a source of contamination, especially if tanks and other parts of the distribution system are not enclosed to prevent entry of foreign matter. Water supply tanks should be constructed of materials that allow for cleaning and should be readily accessible for inspection and testing.

Use of multilinked storage tanks should be avoided if possible, and tanks should not allow water to stagnate. Tanks should be sized according to water usage. In general, a 24-hour maximum storage capacity is recommended, and storage time should be assessed. Occasions have occurred where hotel water storage has been designed to supply water at peak times (morning and early evening time due to shower use by guests), but operationally, the hotel may experience periods of low occupancy. During these times, water has remained in tanks for long periods and promoted *Legionella* proliferation.

As temperature is an integral factor in promoting microbiological activity, cold water supply tanks and piping should be installed such that heat gain is minimized (e.g., do not position close to a heat source, avoid solar gain, and ensure effective insulation). Since it is well documented that dead legs or low flow zones can create a suitable habitat for *Legionella* to proliferate, all such areas within the system should be avoided and those identified removed from the system.

For hot water systems, water heaters bring several engineering issues that have been related to enhanced risk. In a similar way to storage tanks, water heaters should be sized appropriately to meet demand, and be capable of heating contents to the desired temperature throughout. Since this type of equipment is prone to thermal stratification where cooler water tends to be found at the base of the unit, it is recommended that these areas of lower temperature, which are more likely to support the growth of *Legionella*, be avoided or prevented.

Like considerations made to cooling systems, hot and cold potable water systems should be maintained in hygienic condition, free from corrosion debris, scale, and biomass. Water heaters can become scaled and contaminated with debris, and they should be readily accessible for cleaning and inspection. Any debris in the base of the heater should be purged to a suitable drain on an annual basis. Alternatively, point-of-use water heaters with minimal storage and low temperature feed water should be considered as low risk and replacements for water heaters.

If fitted, accumulators should have diaphragms, which are accessible for cleaning since diaphragms have been associated with supporting bacterial growth.

The risk assessment should identify all parts of the system that present a risk. If the risk cannot be eliminated, then a control program is required.

Operational Considerations

The general growth range for *Legionella* is 20 to 50°C (68–122°F). Temperatures in the range of 25 to 42°C (77–108°F) can provide an ideal growth environment, and these temperatures should be avoided, as far as possible, within the hot and cold potable water distribution systems. Climatic conditions may result in water temperature increase, and this effect needs to be considered. To attain hot water with a reduced risk of *Legionella* contamination, water heaters with storage tanks should operate above 60°C (140°F), with hot water distribution giving a temperature of 51°C (124°F) to the point-of-use or tap. Storage capacity and rate of recovery of the water heater should be selected to meet normal fluctuations in demand. Should monitoring identify that high temperatures cannot be maintained due to operating peculiarities or design, then chemical disinfection should be considered as a remedial action.

If a water heater or any substantial part of the system is on stand-by, the water heater and recirculating water temperature should be raised to 60°C (140°F) for at least 1 hour, to reduce the risk of bacterial contamination of the system. This is a form of pasteurization for the water heater. During this period, each outlet should be flushed for five minutes. This technique is known as thermal disinfection.

Cold water supply tanks and cold water services should be maintained at temperatures below 20°C (68°F), where practicable. Hot and cold water pipes should be insulated as needed, but consideration not to insulate piping should be given if insulating piping increases risk of holding water temperatures in the growth range during long holding periods or periods of no water usage. To ensure that cold water remains cold, temperature of the incoming water should be checked at six-month intervals, such that one reading is taken in the winter months and one reading is taken in the summer. Similarly, temperature of the bulk water in the tank should be taken semiannually. Results should be recorded and action taken if temperatures show a marked increase from the norm. Ideally, temperatures below 20°C (68°F) are most suitable to restrict bacterial activity, but in some countries, incoming water is frequently above this temperature. In such cases, use of secondary disinfection should be considered.

Where sections of the system remain unused for long periods, for example an infrequently used shower in a hotel room, steps should be taken to run good quality water through these areas to waste for several minutes, at least weekly or for sufficient time to ensure the whole pipe length has been flushed. However, where sections of a system have not been used or flushed, then it is recommended that a disinfection procedure be performed before use. This process should reduce the risk of exposure to biofilm and possibly *Legionella* that might have colonized the water distribution system. Alternatively, if it is determined that sections of a system are to remain unused for extended periods, for example where staffing levels on-site have reduced the need for outlets, then consideration must be given to isolating these sections and possibly removing piping and fixtures completely.

In an effort to maintain cleanliness, tanks should be cleaned and disinfected if there is visual evidence of accumulation of deposits, sludge, or other contamination. The water surface should be free of deposition, and the tank lid should be in a good condition and fit tightly. An insect/vermin screen should be installed, and thermal insulation should be sound and in good condition.

Review of Control Measures for Hot and Cold Potable Water Systems

Potable hot and cold water systems should also implement a *Program*. This *Program* should detail the control scheme, identify tasks to be undertaken, frequency of the task, and the specific location (often by asset number) of the asset. This allows records to clearly identify what work was done and where.

Earlier in the chapter, the consequence of allowing water to remain still and possibly stagnate was discussed. Water turnover within the tank on a typical day should be monitored annually to ensure that operational changes have not affected water usage. For example, it is common practice for doctors and nursing staff to use alcohol gel to wash their hands between patients. Studies have identified that this practice, primarily introduced to restrict the spread of the methicillin-resistant *Staphylococcus aureus* (MRSA) bacteria, has resulted in less water usage contributing to water age or stagnation. Extra consideration now has to be given to any chance of *Legionella* proliferation within the distribution systems.

Although dependent upon design, internal inspection of water heaters should be undertaken annually, and cleaning and disinfection should be performed if there is evidence of scale or sludge accumulation. Frequently access is limited, and in such cases, water heater temperatures should be checked monthly. Temperatures obtained during thermal disinfection should be checked periodically and results recorded.

In order to ensure that no isolated contamination develops in localized areas of the distribution system, water temperatures of a representative number (e.g., 10–20% of the total number of outlets) should be checked annually on a rotational basis, and a representative number, normally those nearest to and furthest from the water heater, should be checked monthly (so-called sentinel or distal taps). Temperature checks should be taken after running for one minute at full flow for hot taps and two minutes at full flow for cold taps. Hot water temperature should attain more than 50°C (122°F), while cold water temperature should attain less than 20°C (68°F) or < 25°C (77°F), depending on local requirements. This ensures that the whole system is reaching satisfactory temperatures for *Legionella* control.

Thermostatic mixing valves may be used to prevent scalding and considerations should be given to the uses of these devices. Preferably, thermostatic mixing valves should be installed as close as practical to the point-of-use so that hot water can be delivered throughout the entire distribution system at or above 51°C (124°F). Where centralized thermostatic mixing valves are used to reduce water temperature, the blended water temperature should be high enough to maintain a minimum of 51°C (124°F) throughout the distribution system to the point-of-use. However, maximum allowable temperatures may be limited by codes intended to prevent scalding.

Microbiological Monitoring of Hot and Cold Potable Water Systems

Generally, those systems fed with potable water do not require significant microbiological testing. However, such testing forms a useful part of a control scheme, especially if taste or odor problems occur, high temperatures occur in cold water, or correspondingly low temperatures occur in hot water. Where biocides are used as the primary *Legionella* control process and temperatures are reduced, monthly to quarterly *Legionella* samples are recommended to ensure that the control regime is effective. This evidence must be recorded in appropriate site documentation.

In addition to the above recommendations, it would be considered good practice to undertake sampling for both *Legionella* and total heterotrophic aerobic bacteria in systems determined by the risk assessment as high risk. This includes areas such as hospital wards and retirement homes, for example. Testing frequency may be stipulated by local guidance for such premises.

Cleaning and Disinfection of Potable Water Distribution Systems

Cleaning and disinfection of potable water distribution systems are required under a number of circumstances. This procedure may be required in response to visual inspection of water tanks or heaters, temperatures within the system that do not meet recommended control parameters, physical alteration of the system, poor microbiological analysis results, or in an outbreak situation where the risk control program may have been compromised (see Figs. 21.7 and 21.8).

FIGURE 21.7 Poorly controlled system with excessive micro and macro biological growth.

FIGURE 21.8 Contaminated section of system.

When chemical or thermal disinfection is conducted, warning notices must be posted. Physical barriers or tape may be necessary, depending upon site requirements. Chemical disinfection usually is performed using chlorine. In principle, procedures for cleaning and disinfecting new systems or refurbished systems are similar.

Following disinfection, tanks should always be filled with fresh water in order to remove water contaminated with debris.

Records

In legal situations, records are often referred to as “evidence that speaks.” Interpretation of this comment in relation to *Legionella* risk reduction is to infer that any records or communication between different parties should be filed and maintained to provide evidence that a particular issue was addressed. If no records are available, then some governmental regulation bodies might assume the work was never done. Hence, all appropriate records of monitoring and subsequent action should be kept and maintained for at least a five-year period to demonstrate compliance with regulations. Records should be maintained in order to demonstrate effectiveness of the risk management program, for all systems being considered within the risk management plan. Table 21.2 lists typical records that would normally be maintained for a hygiene-based control program.

Records	Content
Risk assessment document and subsequent remedial actions	Consideration of factors such as proliferation potential, aerosol production potential, susceptible populations, and management procedures and corrective actions.
Name and position of people who performed assessment and their qualifications	Details to demonstrate competence.
Water management program for reducing risk	Identification of responsibilities and details on process management.
Details on personnel and lines of communication	Contact details of all management levels and flow diagram for management processes.
Records of plant use	Identification of normal plant operational factors for trend analysis.
Records of work carried out by site or contractors	What work undertaken and by whom.
Defect/action logs, Escalation program	Investigative records and process for deviation from key process indicators (KPI).
System description	Including diagrams and schematic drawings, identification of water supply tanks, inventory of fittings, identification of relevant items of pretreatment plant, and system volume.
Details of inspection procedures	Daily checks on equipment, chemical levels, etc.
Logbook	Records of water temperature, operation of pretreatment plant, inspection and test results, cleaning and disinfection operations, works undertaken on the system, works undertaken as a result of inspections or testing (defect/action log), all signed by the person performing the work.
Training records	To demonstrate competency by knowledge and skills.

TABLE 21.2 Typical Hygiene Records to Maintain

Other Risk Systems

Many water-containing utilities have been identified as a possible source of risk for legionellosis. Decorative fountains, machine coolant systems, and spas are but a few of the systems where potential risk has been identified. In each case, the same basic assessment principles can be applied:

- Does the system contain and support proliferation of *Legionella*?
- Is aerosol production likely?
- If so, who is likely to inhale the aerosol?

Incident analysis after an outbreak situation often identifies critical defects in the risk reduction program. Frequently, repeat nonconformances combine to exacerbate the situation.

Consequence of Outbreak

The worst-case scenario is where exposure has led to illness and possibly fatalities. In such situations, government authorities conduct a thorough investigation to identify any breach of health and safety guidance or where employees and public have been put at risk. In such an event, all records are reviewed in order to determine any lapse in the control plan. A site procedure containing a detailed process to deal with all eventualities is deemed good practice.

Training

Previous outbreaks of Legionnaires' disease have identified a lack of training and understanding of specific requirements needed to ensure that the risk management plan remains effective. Everyone involved in operation and maintenance of cooling water, potable water, and other risk systems should be aware of local guidance, and the need to be able to demonstrate that the individual has been trained to undertake their role in the control process effectively and competently. This includes the requirement for refresher training.

Conclusion

Reducing the risk from exposure to *Legionella* has warranted significant review, such that many countries have produced national guidance on how to introduce, monitor, and record preventative control programs. In addition, WHO has produced a general guidance document to cover many different types of facilities. For each utility, the same process of assessment of risk can be made (e.g., Does the system support the growth of *Legionella?* Does the system produce an aerosol?; Will susceptible people be exposed to it?). By understanding the different interrelating factors that combine to create a risk, and specifically by proactive management, legionellosis can be a preventable disease and exposure to risk reduced.

SECTION 3.5

Applications—Post-Treatment

CHAPTER 22

Primary Effluent Treatment

Industrial effluent treatment systems take many forms, depending on the constituents in the effluent and the goals of the treatment (discharge requirements). Primary treatment, as the name implies, precedes any additional treatment such as biological processes (secondary treatment). The primary treatment may be the only treatment, when the final discharge is to a publicly owned treatment works (POTW), or the treated water meets recycle requirements, such as blast furnace scrubber water in the steel industry. Primary treatment may be preceded by bar screens, grit (sand) removal, equalization basin, and pH correction to protect subsequent equipment and processes.

Effluents contain many different types of organic and inorganic solids, both dissolved and suspended depending on the effluent sources. Physical–chemical processes are used to remove specific dissolved matter in the effluent, such as heavy metals and emulsified oils, and to oxidize or precipitate toxic chemicals. These processes may include sedimentation or dissolved air flotation (DAF).

Clarification by Sedimentation

Clarification of effluent through the process of sedimentation is the separation of suspended solids by gravitational settling. The sedimentation process is used in primary settling basins, removal of chemically treated solids, and solids concentration. Sedimentation basins perform the twofold function of producing both a clarified water product, and a concentrated slurry (sludge) product. Two distinct forms of sedimentation vessels are in common use. The clarifier is used, as the name suggests, for the clarification of a dilute suspension to obtain water containing minimal suspended solids, while producing a concentrated sludge. A thickener is used to thicken a suspension to produce an underflow with a high solids concentration, while also producing a clarified overflow. Primary clarification is the most economical unit process for pollutant removal from a cost per unit weight of biochemical oxygen demand (BOD) or solids removed. For this reason, it is the most widely used process for effluent treatment.

Forms of Solids in Effluent

Total suspended solids (TSS) in water are defined by the U.S. Environmental Protection Agency (EPA) as those dry solids retained on a 0.45 µm filter from a total water sample and reported as dry mg/L or percent dry solids by weight. (The suspended solids include floatable material.) The soluble or dissolved solids in the water are those that pass through the 0.45 µm filter and reported as dry mg/L or percent dry solids by weight. The sum of these two is the total solids in the water. By burning the solids of each, the suspended solids and dissolved solids are further classified into volatile and nonvolatile. The volatile fraction is assumed to represent the organic fraction in the suspended and dissolved solids.

The TSS in the water are additionally divided into settleable solids and nonsettleable solids. The nonsettleable solids are the fine, colloidal particle fraction held in suspension by surface charges that do not settle by gravity. Clarification processes remove only the settleable fraction of the suspended solids. If nonsettleable solids are to be removed by clarification, chemical conditioning (coagulation and flocculation) of the colloidal solids is necessary.

Standard Methods for the Examination of Water and Wastewater (American Public Health Association, Washington, DC) includes two methods for the measurement of settleable solids. The first is reported by volume as mL/L and the second is by weight in mg/L.

A one-liter Imhoff cone is used to settle a mixed sample of the effluent for one hour. The volume of solids that settles in the cone is read by the milliliter graduations on the cone apex. The settleable suspended solids are reported by volume as mL/L.

The nonsettleable solids by weight are measured by settling a minimum one-liter sample in a minimum 90 mm diameter glass vessel. A larger diameter vessel and sample may be used, but the sample depth in the container must be deeper than 200 mm. The sample is allowed to settle for one hour. A 250 mL sample is siphoned from the center of the container at a point halfway between the surface of the settled solids and the water surface without disturbing the settled or floating material. The suspended solids by weight (mg/L) are determined on the 250 mL sample, and this represents the nonsettleable solids. The settleable solids by weight are then the difference between the mg/L TSS and the mg/L nonsettleable suspended solids.

Sedimentation Phenomena

Four basic classes or types of sedimentation processes take place, depending on the particle concentration and the degree of particle interaction. These settling classes are discrete particle, flocculant, hindered (also called zone), and compression (Fig. 22.1). More than one class of settling can take place at any one time, and it is common to have three occurrences in the clarification of dilute solutions. Thickening of solutions having suspended solids concentrations greater than about 500 to 1000 mg/L typically utilizes hindered and compression settling. Table 22.1 describes these types of settling phenomena.

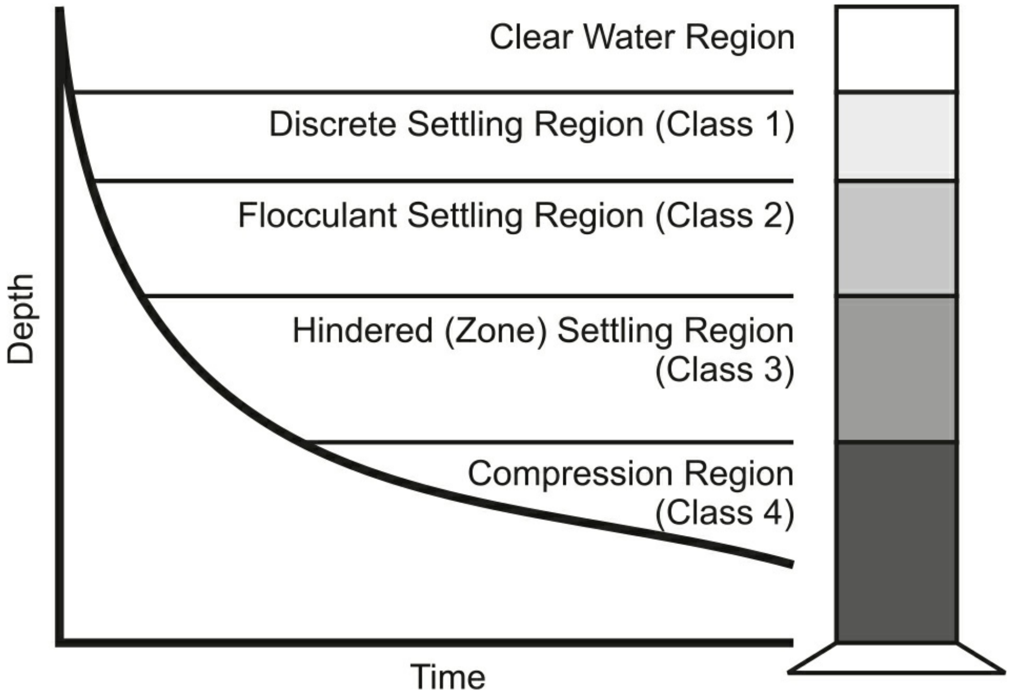


FIGURE 22.1 The four types of settling.

Type of Settling	Description	Application
Discrete particle (Class 1)	Particles in a low solids concentration settle as individual entities not interacting with adjacent particles.	Removal of grit, sand, and inorganic particles such as slag in steel mills.
Flocculant (Class 2)	A dilute suspension of particles that coalesce or flocculate during sedimentation. The particles increase in size and mass by agglomeration, thereby increasing the settling rate.	Most solids in effluent are of a flocculant nature including pulp and paper, food processing, municipal, and biological treatment. Chemically treated solids exhibit Class 2 sedimentation.
Hindered or Zone (Class 3)	Suspensions of intermediate concentration in which the forces between particles are sufficient to hinder the settling of adjacent particles. The particles adhere together, and the mass settles as a blanket, forming a distinct interface between the floc and the supernatant. The settling rate starts to decrease.	Hindered settling is characterized by biological solids and flocculated chemical suspensions, when the concentration exceeds 500–1000 mg/L, depending on the type of particle.
Compression (Class 4)	The particle suspension has reached a concentration such that a structure is formed and further settling can occur only by compression of the structure. The weight of the particles being constantly added to the top of the structure by sedimentation provides this compression. The settling rate of this zone becomes very slow.	Occurs in the lower layers of deep sludge masses, such as in the bottom of deep clarifiers and in sludge-thickening facilities.

TABLE 22.1 Types of Sedimentation in Effluent Treatment

Discrete Particle Settling

The analysis of discrete, nonflocculating particle settling is by means of the classic laws of sedimentation formed by Newton and Stokes. Newton's Law relates the gravitational force on the particle, with the frictional resistance or drag, and the difference between the densities of the particle and liquid. The value of the drag coefficient varies depending on turbulent or laminar flow conditions and is a function of the Reynolds number. The drag coefficient becomes a constant for the low laminar flow conditions found in clarification. Stokes incorporated this constant drag coefficient into Newton's gravitational force equation to arrive at the classic Stokes' Law for sedimentation:

$$V_o = \frac{G(\rho_1 - \rho_2)D^2}{18\mu} \tag{22.1}$$

where V_o = settling velocity, cm/s
G = gravitational force, $\mathrm{cm/s^2}$
ρ_1 = particle density, $\mathrm{g/cm^3}$
ρ_2 = liquid density, $\mathrm{g/cm^3}$
D = particle diameter, cm
μ = liquid viscosity, $\mathrm{dyne \cdot s/cm^2}$

A terminal velocity V_o is selected for the sizing of a sedimentation basin so that all particles having a velocity equal to or greater than V_o are removed. Class 1 settling in an ideal basin is shown in Fig. 22.2. The particle having a settling velocity V_o that settles through a distance equal to depth D in length L (theoretical detention period) is removed. This is called the basin overflow rate:

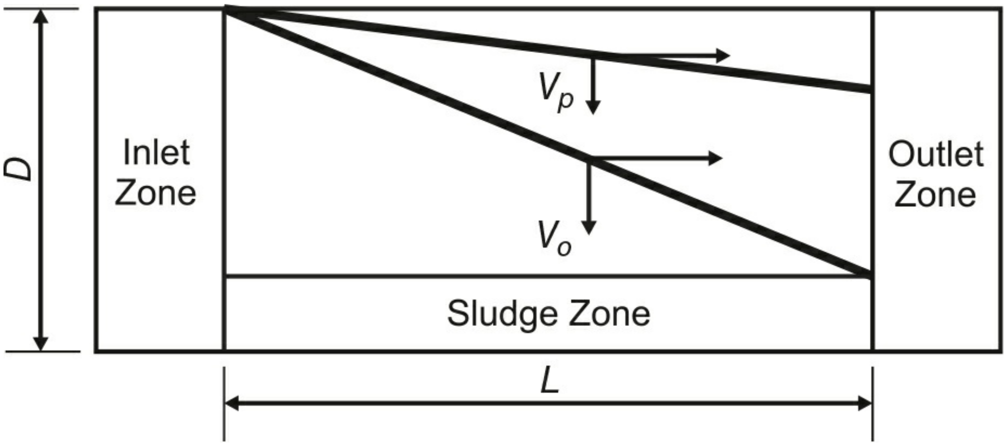


FIGURE 22.2 Discrete particle settling.

$$V_o = \frac{Q}{A} \tag{22.2}$$

where Q = inlet flow rate, gpm or gpd (m^3/h)
A = surface area of tank, ft^2 (m^2)
V_o = overflow rate, gpm/ft^2 or gpd/ft^2 (m^3/[h · m^2] or m/h)

In the ideal basin of Fig. 22.2, it is assumed that particles entering the tank are evenly distributed over the inlet cross-section, and a particle is considered removed when it enters the sludge zone. Thus, all particles with a settling velocity greater than V_o are removed, and particles with lower settling velocity (V_p) are removed in the ratio V_p/V_o as illustrated in Fig. 22.2.

The flow capacity of basins for discrete particle settling is independent of depth, as shown in Eq. (22.2). The length of the basin and the time that a unit of water is in the basin for continuous flow sedimentation needs to be such that all particles with the design velocity of V_o settle to the bottom. The design velocity V_o for a full-scale continuous flow clarification device must be adjusted for the effects of influent and effluent turbulence, hydraulic short-circuiting, sludge storage, velocity gradients due to temperature changes, and operation of sludge removal equipment.

Flocculant Settling

Flocculant settling is created by the coalescence of particles in a dilute solution. The settling velocity of the particle increases as it settles through the tank depth, because of this agglomeration that increases its size and density. Figure 22.3 illustrates the curvilinear settling path of the particle as it increases in settling velocity and size. Most of the suspended solids in industrial effluents are flocculant in nature. The efficiency of removal for discrete particles is related only to the overflow rate, while flocculant particle removal is dependent on both overflow rate and depth of basin (detention time).

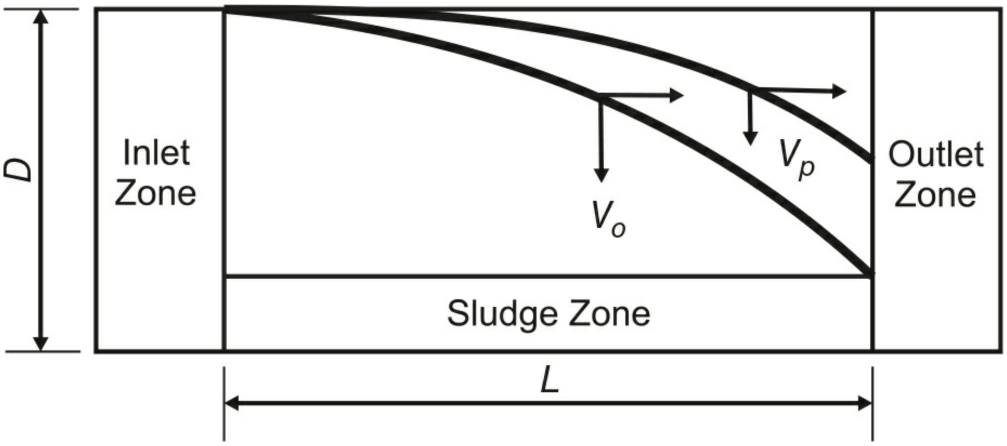


FIGURE 22.3 Flocculant settling.

The degree of flocculation that takes place is dependent on the opportunity for particle contact, the overflow rate, the depth of basin, initial particle concentration, range of particle sizes, and flocculating nature of the particles. A mathematical analysis concerning these parameters for basin design and operation is generally considered impossible. Long column settling tests are required to determine the effects of these variables, when historical data concerning the type of solids in a specific type of effluent is unknown. The columns used are typically 6 inches (152 mm) in diameter by 8 to 10 ft (2.4–3 m) high.

Hindered Settling

Hindered settling is typified by activated (biological) sludges and chemically flocculated suspensions, when the concentration of solids exceeds 500 to 1000 mg/L. Hindered settling takes place following the concentration of the suspension during flocculant settling or in gravity thickening, when the initial solids concentration is greater than about 500 mg/L. Since flocculated particles are in close proximity to each other, they settle as a mass or blanket, and form a distinct water/solids interface at the top of the blanket. The friction produced as the water moves up through the interstices of the blanket slows the settling rate of the mass (Fig. 22.4). The reduction in settling rate continues as the solids blanket concentrates. The rate of settling in the hindered region is a function of the concentration of solids and their characteristics.

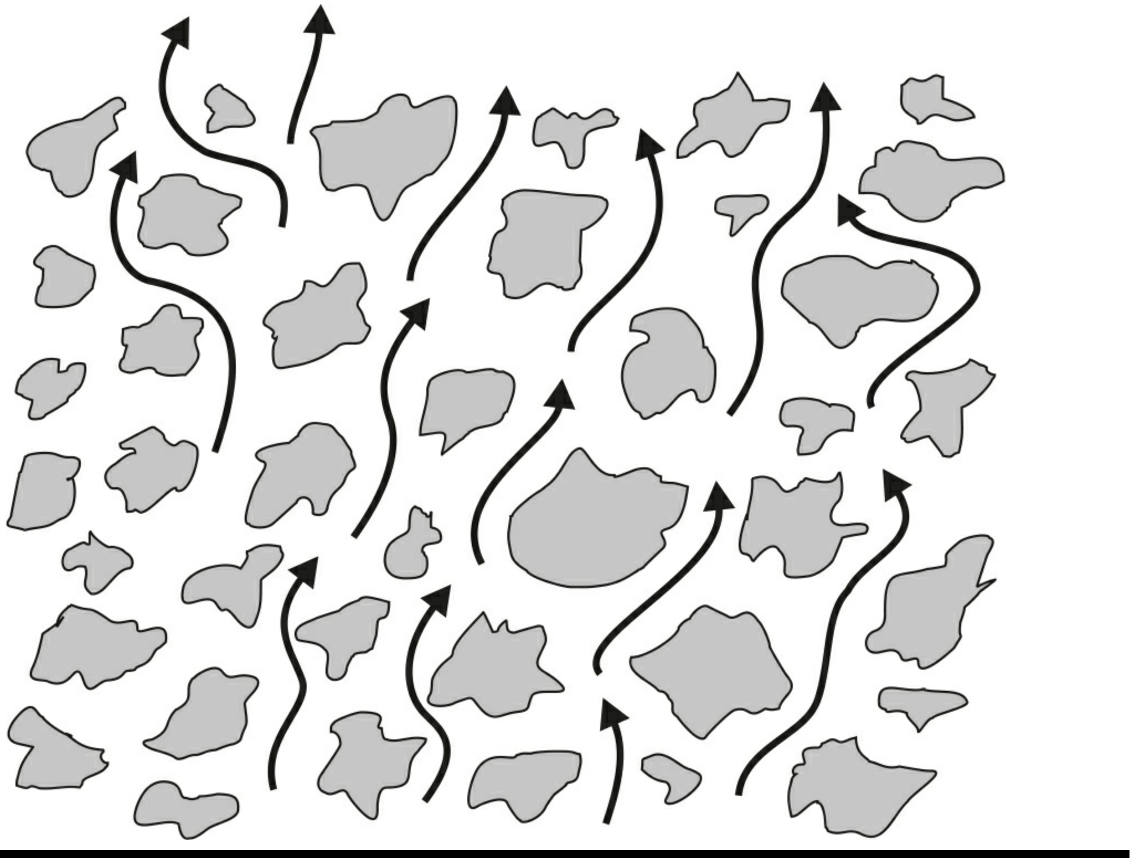


FIGURE 22.4 Hindered settling.

Compression Settling

A compressed layer of solids starts to form beneath the hindered settling zone as sedimentation continues. A structure is formed in this region by the close physical contact between the particles. Additional water is forced out and upward from the hindered settling zone, by the increasing weight of solids on the top of the zone as sedimentation continues. The maximum solids concentration of the solids at the bottom is limited by the characteristics of the solids and the weight of solids above the lowest layer.

Due to the many variables between the various types of solids encountered in effluent treatment, settling tests are usually required to determine the settling rate and detention time when hindered and compression settling are a consideration. The test cylinder is equipped with a slow-speed stirrer rotating at 4 to 5 revolutions per hour. The stirrer simulates the rake action and corresponding hydraulic motion in a clarifier. This breaks the arching action of the solids in these zones, to increase the release of water from the sludge bed, and increase solids concentration (Fig. 22.5).

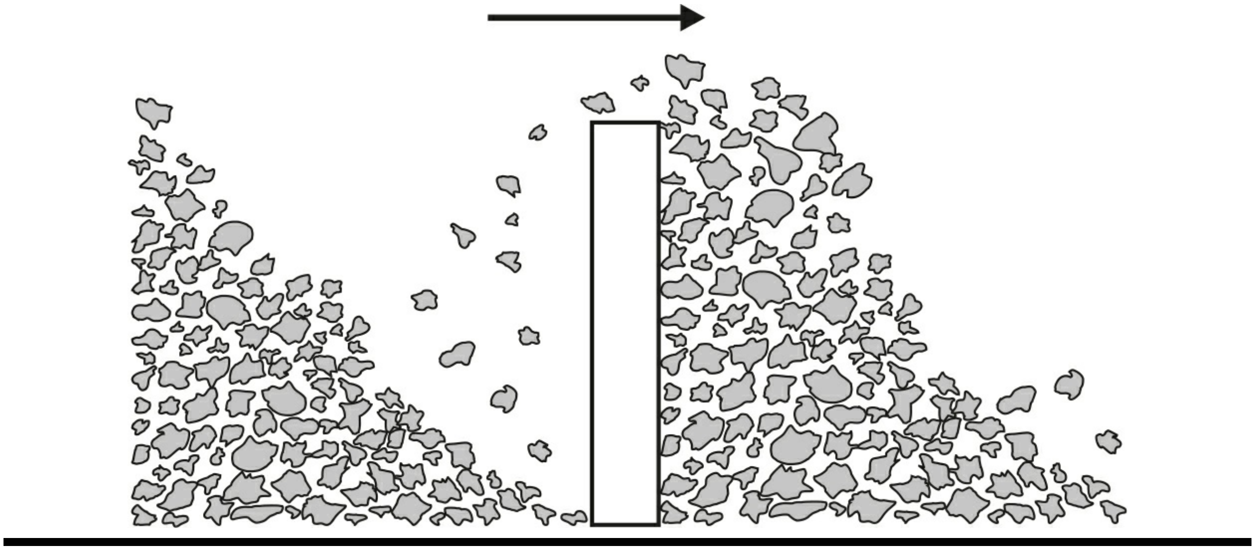


FIGURE 22.5 Rake action in compression zone.

Mass Loading

Both the clarification of the water overflow and the thickening of the sludge underflow are involved in the separation of flocculant suspensions. The overflow rate for clarification requires that the rise in velocity of the liquid overflowing the tank be less than the settling rate of the suspension. The tank surface area requirements for thickening of the underflow to a desired concentration are related to the solids loading or solids flux, usually expressed in terms of mass loading (pounds per square foot per day or kilograms per square meter per day) or a unit area (square feet per pound of solids per day or square meters per kilogram of solids per day). The mass loading with corresponding underflow concentration for a particular application can be calculated from a stirred laboratory test.

In most clarification applications, the limiting flux and underflow concentration from the laboratory, testing must be equal or be greater than the solids loading rate to the clarifier:

$$G_L = \frac{C_o Q_o}{A} = \frac{M}{A} \tag{22.3}$$

where Q_o = influent flow, ft^3/d (m^3/d)
C_o = influent solids, lb/ft^3 (kg/m^3)
M = solids loading, lb/d (kg/d)
G_L = limiting solids flux, $\text{lb}/[\text{d}\cdot\text{ft}^2]$ ($\text{kg}/[\text{d}\cdot\text{m}^2]$)
A = area, ft^2 (m^2)

Both gravity and the velocity resulting from sludge removal at the tank bottom in a continuous clarifier or thickener remove solids:

$$U = \frac{G_L}{C_u} \tag{22.4}$$

where U = downward sludge velocity due to sludge removal, ft/d (m/d)
C_u = underflow concentration, lb/ft^3 (kg/m^3)

Increasing the underflow pumping rate U in Eq. (22.4) decreases the underflow concentration C_u. The solids flux G_L is not the limiting factor for most clarification applications, since the influent suspended solids are generally less than 500 mg/L.

Clarifier Hydraulic Capacity

The parameters that affect the settling rate are of prime consideration for the sizing and operation of a sedimentation device. The larger the particle diameter, and the heavier the particle, the faster it settles. The colder the water (higher viscosity), the slower the settling rate. Effluents contain a mixture of particle sizes and densities. Therefore, the sedimentation device should be sized for the smallest, lightest settleable particle, in order to maximize the settleable solids capture. Conversely, a change in an industrial process to one that produces a larger quantity of smaller lighter particles results in a decrease in solids capture.

A sedimentation device that includes inlet baffling for the dissipation of the influent energy, a quiescent zone for particulate settling, mechanical means for the removal of settled solids, and low flow velocity to the outlet, is commonly called a clarifier. The hydraulic capacity of a clarifier is based on the discreet and flocculant type settling velocity expressed as feet per minute (meter/hour). In US units, multiplying the settling rate by 7.48 gal/ft^3 yields the hydraulic loading expressed as gallons per minute per square foot. The hydraulic loading can also be expressed as gallons per day per square foot. The metric units are cubic meters per hour or day per square meter. This hydraulic loading is also called the overflow rate, and it is used to size a new clarifier or ascertain the capacity of an existing clarifier.

A settling curve is developed for a sample of the effluent to arrive at an estimate of the overflow rate. Preferably, a minimum two-liter graduate is used for the settling test, and the fall of the suspended solids in milliliters is recorded for each 30 seconds of elapsed time. Readings are taken for at least 30 minutes or until the change in solids height per minute is relatively small or constant. The results in milliliters are converted to inches (millimeters) by measuring the graduate (inches/2000 mL or mm/2000 mL) and graphed as illustrated in Fig. 22.6. The slope of the linear portion of the curve is the settling rate for that sample in inches per minute (mm/min).

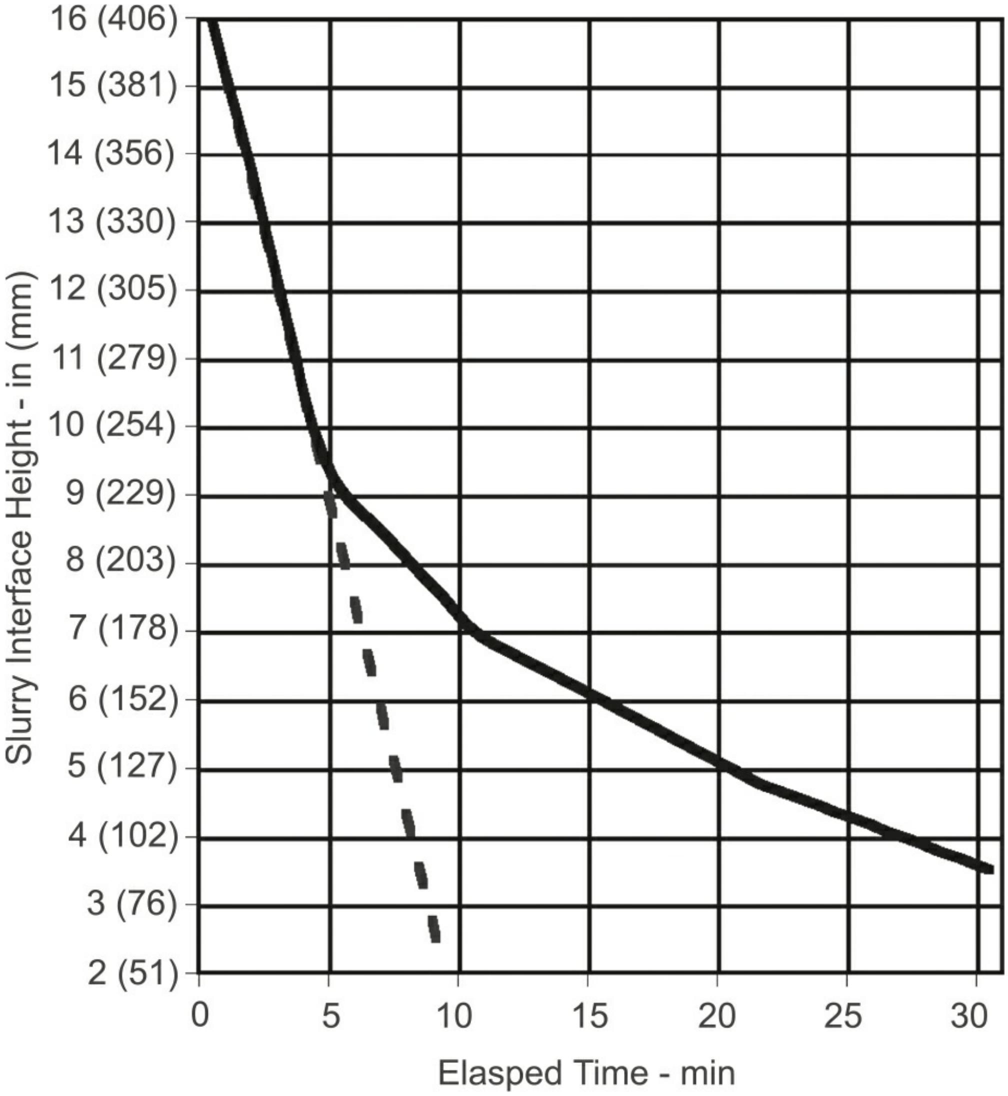


FIGURE 22.6 Settling curve.

In the Fig. 22.6 example, the slope is (2–16)/(9–0) = –1.56 inches/min (–39.51 mm/min) yielding a negative slope as it should be when we are measuring the fall of suspended solids. In our hydraulic loading calculation below, we will be using the absolute value of the slope for the calculation. It is necessary to apply a scale-up factor to account for the dynamics of an operating clarifier versus the quiescent state of the settling test. The scale-up factor is generally in the range of 0.65 to 0.85, depending on the actual application conditions. The hydraulic loading can then be calculated as follows:

US Units (1.56 in./min)(1 ft/12 in.)(7.48 gal/ft^3)(0.7) = 0.68 gpm/ft^2 or 980 gpd/ft^2

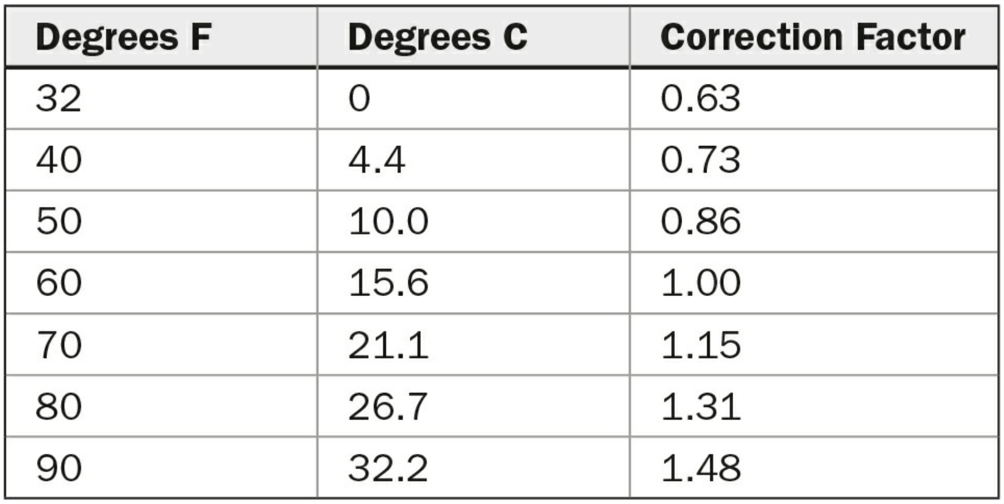
Metric Units (39.51 mm/min)(1 m/1000 mm)(60 min/h)(0.7) = 1.66 m^3/[h · m^2] or 39.8 m^3/[d · m^2]

The sedimentation device can be referred to as a clarifier-thickener, when thickening of the settled sludge is desired. Determining the settling rate of the sludge bed to achieve the target sludge concentration is important to learn if this rate controls the capacity of the clarifier-thickener. The dry solids loading or solids flux, expressed as pounds dry solids per square foot per hour or day (kilograms dry solids per square meter per hour or day), is the parameter used to describe the thickening capacity. (A typical example is a secondary clarifier following a biological aeration basin, where the solids loading and not the hydraulic loading is the controlling factor.) The concentration of the settling sludge bed takes place during and after the knee in the settling curve (Fig. 22.6), where hindered and compression zone settling take place. Generally, the solids flux is not a controlling factor in clarification of effluents having dilute solids concentrations less than about 500 to 1000 mg/L.

Another major parameter for sizing a clarifier is the minimum tank depth or detention time. The tank volume must provide the required flocculant settling depth plus 3 to 4 ft (0.91–1.2 m) for deceleration of the water as it approaches the effluent weirs, plus depth for sludge storage. The water depth at the tank wall is commonly 8 to 15 ft (2.4–4.6 m), with a minimum basin floor slope of 1 on 12. The typical detention time is in the range of 1.5 to 3 hours. Slow-settling solids usually require a deeper water depth with correspondingly longer detention times.

Temperature

Warm water has a lower viscosity (less dense) than colder water. Therefore, the particle settling rate is faster at higher water temperatures than colder ones. Raising the temperature from 32 to 80°F (0–27°C) doubles the settling rate for a given particle, since both the density and viscosity of the water are reduced. Multiply the rise rate by the correction factor in Table 22.2 to adjust for the change of water temperature from 60°F (15.6°C).



Degrees F	Degrees C	Correction Factor
32	0	0.63
40	4.4	0.73
50	10.0	0.86
60	15.6	1.00
70	21.1	1.15
80	26.7	1.31
90	32.2	1.48

TABLE 22.2 Temperature Correction for Rise Rate

Another temperature concern is the possibility of developing thermal gradients within the clarifier. If developed, they can prevent the sedimentation of the suspended solids or lift settled solids, from the sludge blanket up to the outlet launders. This is of concern when treating warm waters in above grade steel tanks, in cold climates. The water at the tank wall and floor cools, so that the bottom of the tank has a colder water temperature then the incoming water. The warmer influent water can short-circuit to the effluent launders, resulting in high solids carryover. In warmer climates, above ground clarifiers can absorb radiant heat from the sun, and clarifier water temperatures increase. When cooler influent water enters the clarifier, the temperature difference can create thermal currents, which can result in resuspension and carryover of settled floc.

Clarifier Operating Principles

The operating zones in a clarifier are a zone of clear water, the sedimentation zone (discrete and flocculant settling), and the thickening zone as illustrated in Fig. 22.7. The depth of the thickening zone (sludge bed) is dependent on the depth of the tank allocated for sludge thickening. The water inlet must always be above the sludge bed (thickening zone) for high efficiency solids capture. Solids can be carried to the outlet launder, if the feed goes through the top of the sludge bed. The objective is to operate the clarifier with as low a sludge bed depth as possible, yet still produce a high underflow sludge solids concentration, if needed.

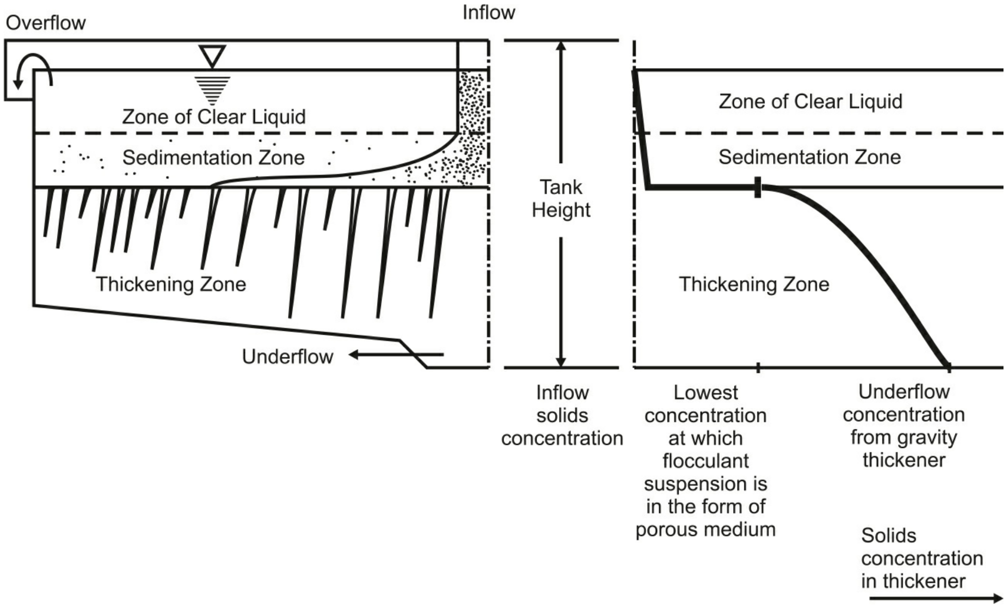


FIGURE 22.7 Clarifier operating zones.

The solids mass balance around the clarifier must be maintained at all times. The influent settleable dry solids less, the effluent settleable dry solids, plus the underflow dry solids, must be zero, to keep the continuous operation of the clarifier in balance. The required underflow sludge pumping volume can be estimated by the influent settleable solids, less the effluent settleable solids in mL/L times the influent flow.

The solids inventory (sludge bed) in the clarifier becomes greater with an increase in the influent solids, or a decrease in underflow pumping. If not corrected, this imbalance results in an increase in the effluent solids. For example, plants that store sludge in the clarifier to meet an eight-hour per day sludge dewatering schedule classically have increased effluent solids when not dewatering. Likewise, trying to store sludge in the clarifier over a weekend can be disastrous, particularly if the settled solids contain organic material. The organic material can undergo anaerobic decomposition producing methane and hydrogen sulfide gases, which can float the settled solids. Organic solids should not be kept in the clarifier longer than 24 hours.

Sludge Bed Depth Measurement

Regular measurement of the sludge bed depth is an easy way to maintain the clarifier solids balance. An increase in sludge bed depth indicates that the underflow blowdown needs to be increased, while a decreasing depth shows that the underflow pumping can be decreased. The best operation is one that can pump the underflow continuously to subsequent sludge handling facilities, instead of an on/off pumping schedule.

The sludge bed depth can be measured manually using a sludge judge. This is a clear plastic tube having feet or meter graduations with a check valve at the bottom. A core sample of the sludge bed is taken with the sludge judge and the depth of the sludge read on the side of the tube. This measurement always should be taken at the same place on the clarifier walkway or wall, since the floors of clarifiers are generally on a slope.

Automatic sludge bed indicators are also available. Some are a probe type based on the transmission and receiving of an infrared beam, while others are based on sonics. The sonic transmitter and receiver are located at the water surface, and the face of the instrument's control panel indicates the profile of the clarifier depth and sludge bed, much like a fish finder. The infrared types of indicators do not work in situations where the water is highly colored. Either type of indicator can be used to automatically control the underflow pumping, to continuously keep the sludge bed depth and thus the solids balance, in the optimum range.

The rake drive torque can be used as a surrogate for the sludge bed depth in large clarifiers handling settleable solids with a high specific gravity, such as in the steel and paper industry. The rake drive torque usually goes up as the sludge bed depth increases. The motor amps cannot be used for the bed depth indication, since the rake drive unit is geared down to such a low speed.

Influent Flow Control

Continuous measurement and recording of the influent flow to a clarifier indicate the instantaneous hydraulic loading and changes with time. Flow rates greater than the design overflow rate result in an increase in the effluent solids. Rapid, short-term, large increases in the flow rate need to be avoided, since the resulting hydraulic surge can wash solids out of the clarifier. It may take a clarifier as long as two hours to recover from such a surge.

Effluent discharged to the primary clarifier is often quite variable, due to storm water and intermittent discharges from an industrial plant. An equalization basin is often provided to even out these variations in both flow and composition. The most efficient solids removal occurs when constant flow is treated within the clarifier's design rating.

On/off level switches may control the forwarding pumps from the equalization basin or the pump station wet well, which is poor practice. The influent pumps need to be controlled to eliminate the clarifier surging created by this on/off control. One method is to use a modulating valve that is controlled by the basin or wet well level that regulates the pump discharge directly to the clarifier, or recycles a portion of the flow back to the basin or wet well in order to keep the clarifier influent close to a constant rate. Another method for multiple pumps is to have a baseline constant speed pump or pumps in conjunction with a variable speed pump or a third pump, which has a modulating discharge throttling valve. The pump speed or discharge throttling valve is adjusted proportionally to the level in the wet well or equalization basin, so that the clarifier influent flow rate is gradually adjusted to eliminate high peak flows while maintaining the hydraulic loading within the design value.

Hydraulic devices such as overflow weirs and gates must divide the flow equally to multiple clarifiers. One clarifier in the group can become hydraulically overloaded with a poor division of the total flow. Dye or diagnostic TRASAR® chemistry tests can be used to check and adjust flow distribution.

Chemical Treatment

Chemical treatment of the clarifier influent can be used to increase removal of suspended solids, by flocculating the colloidal nonsettleable solids to convert them to settleable ones. Depending on the degree of overloading, problems associated with high hydraulic or solids loading can be alleviated by chemical treatment.

Coagulants and/or flocculants may be used, depending on the industry and the goals of the chemical treatment. The coagulants may be inorganic salts, such as iron or aluminum, organic polymers having various formulations, or a blend of organic and inorganic. Anionic, nonionic, or cationic polymer flocculants are used alone or following a coagulant. The polymer flocculants are available in different molecular weights for each charge family. Polymer flocculants, besides increasing the clarity of the effluent, may also increase the underflow sludge concentration, depending on the chemical dosage.

The appropriate chemical program for a specific installation is ascertained by jar testing. The coagulant, if used, is generally added upstream from the clarifier at a point with high energy mixing, such as the suction side of the clarifier feed pump. The long molecular chain flocculants cannot withstand high energy mixing, since the molecular chain can be sheared. The flocculant is typically added just outside the clarifier or into the clarifier feed well.

Types of Sedimentation Clarifiers

Circular, rectangular, plate (also called lamella), drag, and oil/water separators are the basic types of sedimentation clarifiers. The parameters previously discussed in general for sedimentation pertain to these units.

Circular Clarifiers

Circular center-feed clarifiers are the most common sedimentation configuration. Figure 22.8 illustrates the side inlet, bridge supported clarifier mechanism used for basins smaller then approximately 50 ft (15 m) in diameter. For basins 50 to 200 ft (15–61 m) in diameter, the clarifier mechanism is supported by a centrally located column, with the inlet pipe being beneath the floor and rising up through the column to the feed well. The center-feed clarifier has four distinct sections, each with its own function.

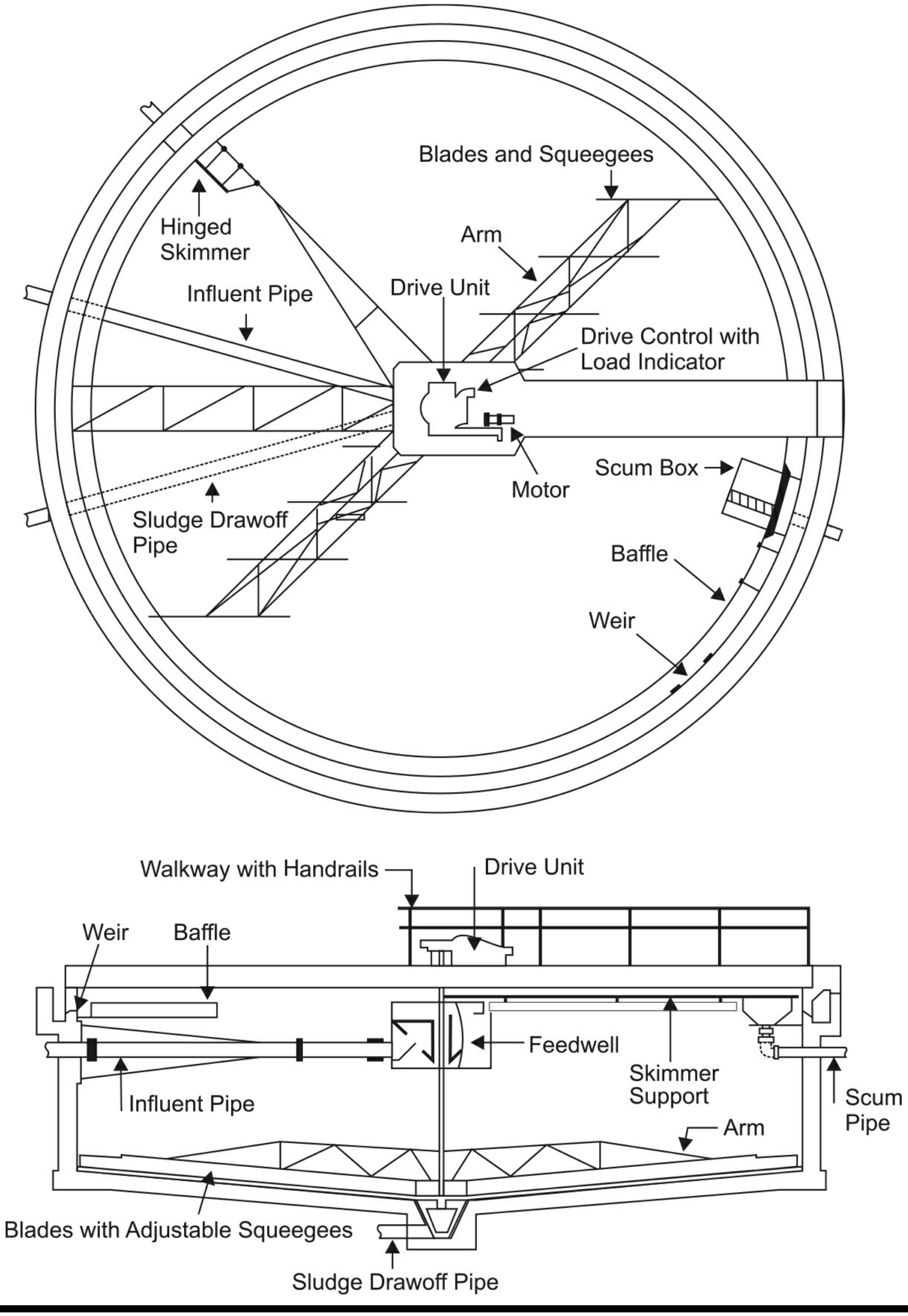


FIGURE 22.8 Center-feed clarifier. (*Courtesy of Envirotech.*)

The inlet section or feed well of the center-feed clarifier provides a smooth transition from the high influent velocity to the low uniform velocity required in the settling zone. The feed well must be carefully designed to provide the necessary water velocity reduction to prevent turbulence and short-circuiting in the settling zone, with resulting solids carryover. The quiescent settling zone must be large enough to meet the overflow rate and depth requirements for discrete and flocculant settling.

The outlet zone provides a transition from the low velocity of the settling zone to the relatively higher outlet velocity, which is typically limited to values less than 14 gpm per linear foot (10.4 m^3/h per linear meter) of outlet weir plate. Treated water is typically discharged over v-notched weir plates, which serve two purposes. The v-notched weirs provide equal removal of the water from 360° of the periphery of the circular clarifier. The v-notches also maintain the water surface elevation in the clarifier close to constant for varying flow rates, which allows floating material to be skimmed from the surface.

The fourth section, the sludge zone, must effectively collect and compact the solids removed in the settling zone and remove this sludge from the clarifier without disturbing the sedimentation zone above. The floor is normally sloped at 1 on 12 to the center of the unit, where sludge is collected in a hopper for removal (blowdown). Mechanically driven sludge rakes or plows move the sludge down the slopping floor to the sludge hopper. The rakes are commonly driven from a drive unit located at the center of the tank. Another less frequent configuration uses a traction drive mounted on the top of the basin wall, which drives a rotating walkway that rotates the rakes and skimmer.

The peripheral-feed (rim-feed) clarifier (Fig. 22.9) attempts to use the entire volume of the circular clarifier basin for sedimentation. The influent trough width decreases from the influent location to a point 180° away, and has orifices in the floor spaced to distribute the flow equally around the tank periphery. Water enters the lower section at the periphery at extremely low velocity, providing immediate sedimentation of large particles. The velocity accelerates toward the center, and then decreases as the flow is reversed and redirected to the overflow weirs on the effluent trough, located inboard of the influent launder. This type of clarifier is sensitive to temperature changes and hydraulic load fluctuations, since the flow pattern depends entirely on inlet hydraulics.

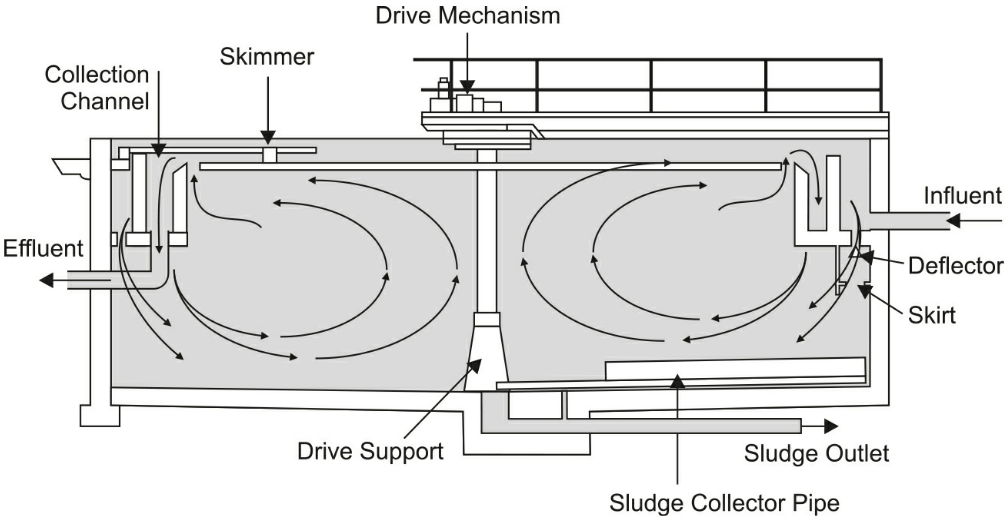


FIGURE 22.9 Peripheral-feed clarifier. (*Courtesy of Envirex, a Rexnord Company*.)

Rectangular Clarifiers

The rectangular basin is somewhat like a section taken through a center-feed clarifier, with the inlet at one end and the outlet at the other. A typical rectangular basin has a length to width ratio of approximately 4:1. Flow through rectangular clarifiers enters at one end, passes through an inlet baffle arrangement, and traverses the length of the tank to the effluent weirs and troughs. Sludge removal is normally accomplished by a dual-purpose flight system (Fig. 22.10). The rake mechanism consists of two, parallel endless conveyor chains running the length of the basin, with rake flights (cross pieces) extending across the width of the tank attached between the chains. The settled solids are moved by the flights to the sludge hopper, typically located at the influent end of the basin. The flights on their return travel to the effluent end, serve as skimmers to remove floating material. The flight system moves very slowly to avoid turbulence, which could interfere with the settling process. The rotating scum trough removes floating material. The trough may be either manually operated or automatically rotated to remove the floatable material that accumulates at the lip of the skimmer. The chain and flight mechanism design limits the width of this type of rectangular clarifier to about 20 ft (6.1 m). Common walls can be used between multiple units to reduce construction costs (Fig. 22.11).

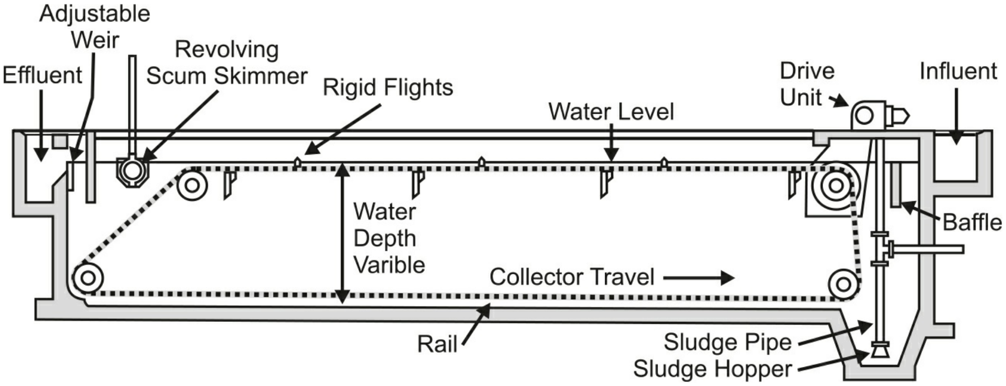


FIGURE 22.10 Rectangular clarifier.

FIGURE 22.11 Rectangular clarifiers with common wall construction and traveling bridge collectors. (*Courtesy of Walker Process Division, Chicago Bridge & Iron Company*.)

A single sludge scraper supported by a traveling bridge is used to move the sludge in wide rectangular basins. The bridge moves on rails mounted on the tank walls (Fig. 22.12). The bridge may be towed by cables or powered by a traction drive mounted on the wall. A skimmer is also supported from the bridge to move floating material to the scum trough that may be located at either the influent or the effluent end. The bridge and skimmer move material only in one direction and are retracted for the return trip to the opposite end.

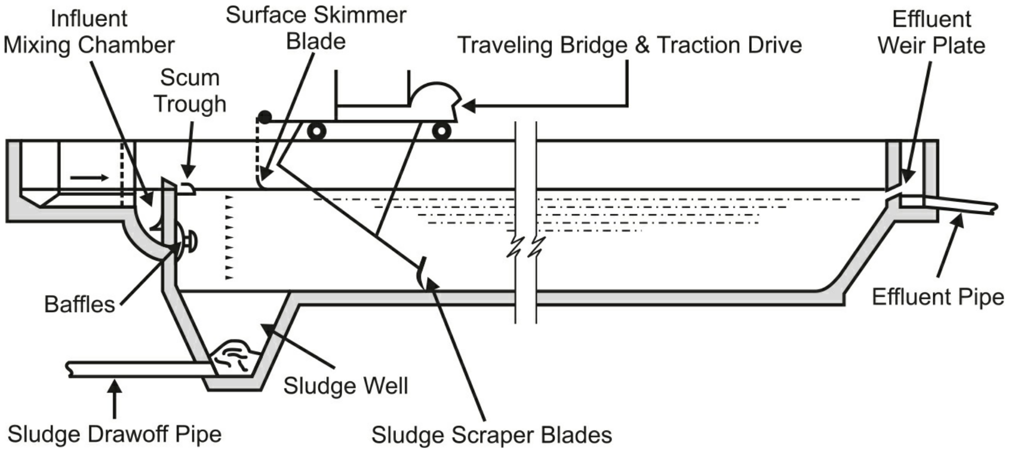


FIGURE 22.12 Traveling bridge mechanism.

The traveling bridge is generally provided with a programmable controller for the traveling cycles of the bridge. For example, the bridge may scrape the sludge in the first third of the basin two or three times (where a large quantity of solids settle), and then scrape the total basin length, then returning to the opposite side, and resting for a period before starting the cycle again. The best traveling cycle time is dependent on the type of effluent and the solids characteristics.

Settled solids may be collected in a single hopper, multiple hoppers, or in a transverse trench which has a hopper at one end for either the chain and flight, or traveling bridge sludge removal mechanism. The transverse trench may be equipped with a chain and flight collector or a screw conveyor to move the sludge to the hopper.

Circular sludge rake mechanisms are designed with pantograph extensions, so that the mechanism can rake the corners of a square basin. Two of these mechanisms are then used to remove sludge in rectangular basins (Fig. 22.13).

FIGURE 22.13 Circular sludge collector with rakes designed for corner cleaning. (*Courtesy of FMC Corporation.*)

Parallel Plate and Tube Clarifiers

Prefabricated clarifiers that incorporate parallel plates or tubes on a slope are commonly used for smaller plant flow rates [less than about 1000 gpm (227 m^3/h)]. Figure 22.14 illustrates the Parkson Lamella® clarifier that incorporates a flash mix tank and a flocculation tank. The flow is introduced by means of a feed duct from the flocculation tank to the clarifier feed box, which is a bottomless channel between the plate sections. The flow is then directed downward to the individual side entry plate slots. The feed is distributed across the width of the plates and then flows upward under laminar flow conditions. The solids settle on the plate surfaces, while the clarified water exits from the top of the plates through orifice holes. These holes are placed immediately above each plate and are sized to induce a calculated pressure drop to ensure that the influent flow is evenly distributed among the plates. The solids slide down the plate surfaces into the sludge hopper, from where the sludge is removed. Flocculation is induced as the solids roll down the inclined surface.

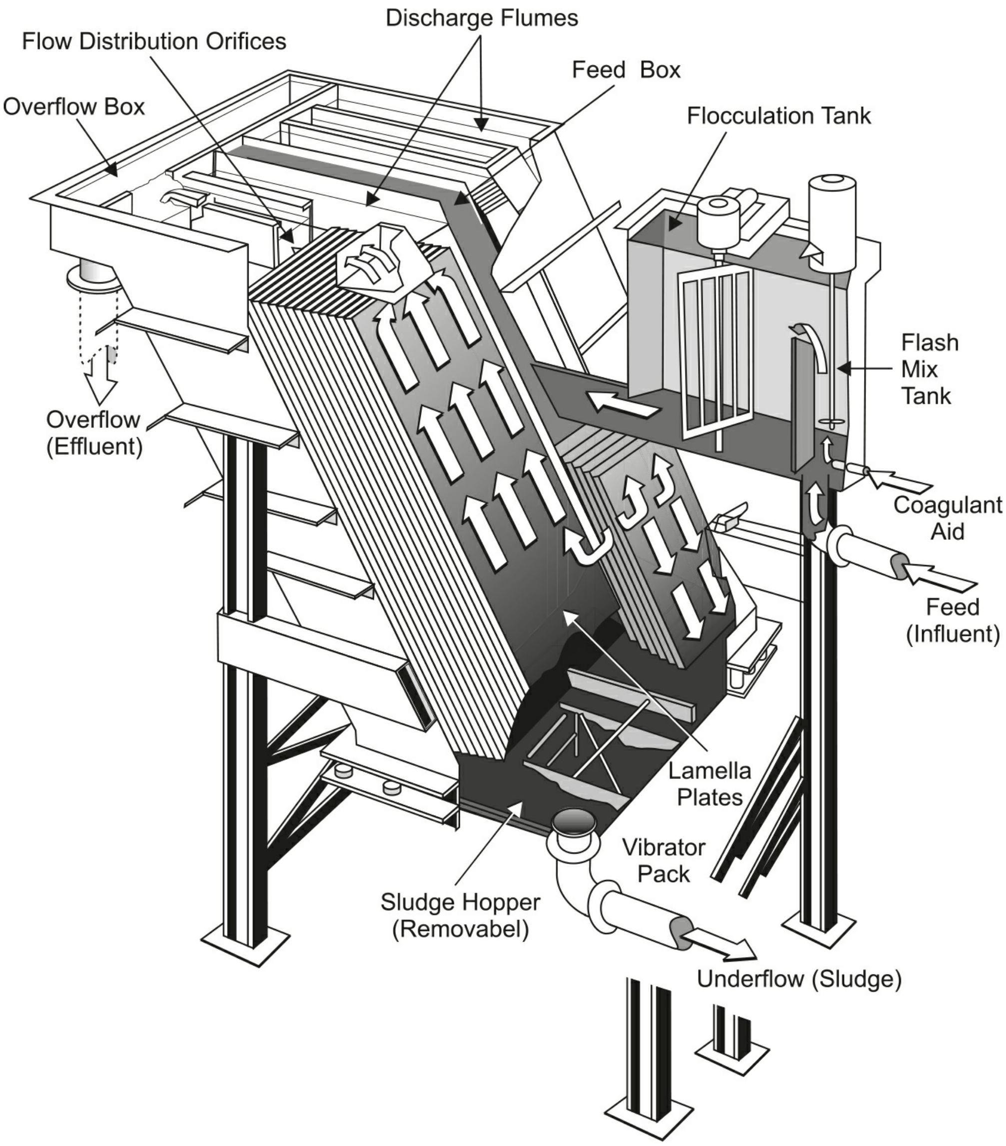


FIGURE 22.14 Parkson Lamella® clarifier. (*Courtesy of Parkson Corporation*.)

The plates are spaced 2 to 4 inches (51–102 mm) apart and inclined 45 to 60° from horizontal, depending on the application and manufacturer. The total effective settling area is based on the horizontal projected area of each plate (Fig. 22.15). The total projected area is used to calculate the rise rate. The design rise rate for plate clarifiers is the same as for conventional clarifiers. The only advantage that a plate clarifier has over a conventional clarifier is that a large horizontal settling area can be provided in a small area of land or footprint. Figure 22.15 illustrates the area used for a plate clarifier as compared to the same area provided by a conventional rectangular clarifier. Some manufacturers use sloped parallel tubes instead of parallel plates, in which case the tube modules are referred to as tube settlers. The sedimentation principles for tube settlers are the same as for the parallel plate configuration.

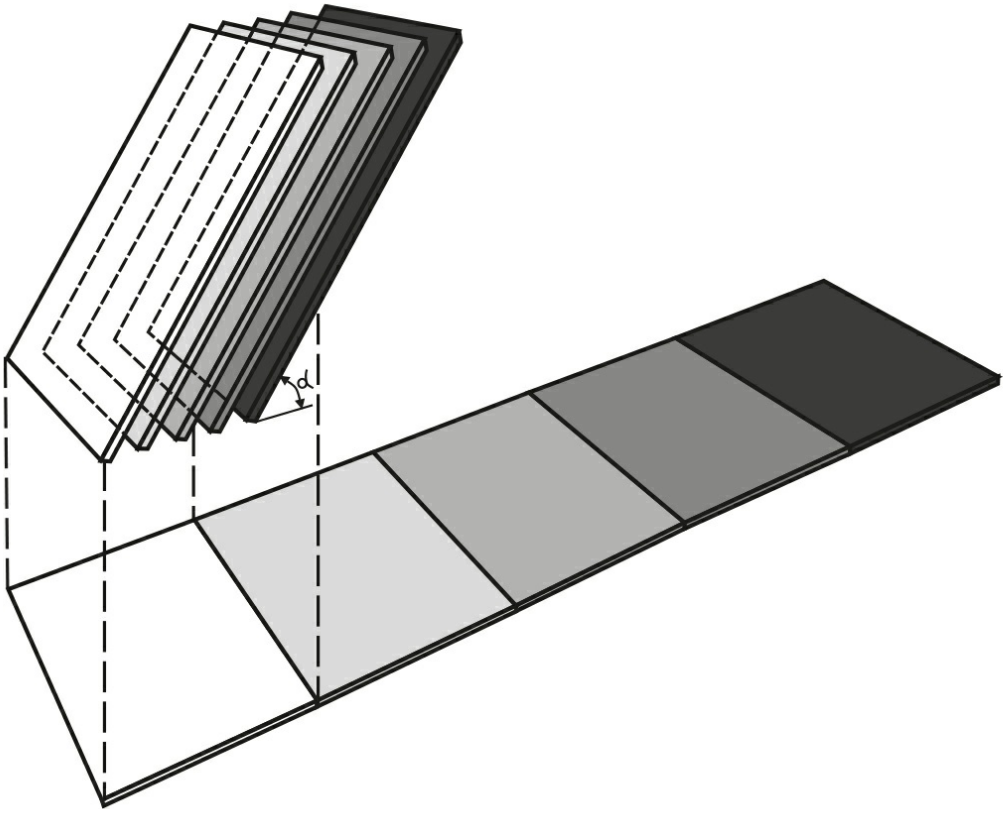


FIGURE 22.15 Plate clarifier floor area compared to a conventional rectangular clarifier.

Parallel plate sedimentation is based on both discrete and flocculant particle settling, and the overflow rate for the total plate projection area is determined by settling tests, the same as for conventional type clarifiers (Fig. 22.16). The parallel plate arrangement does not provide the necessary area and depth for hindered or compression settling. Its application is therefore limited to dilute suspensions having a maximum suspended solids concentration of approximately 500 to 1000 mg/L, depending on the application. The plate surfaces may have to be periodically cleaned, if the solids have a sticky nature and adhere to the plates. The accumulation of solids on the plate surfaces results in solids carryover, due to increased water velocity.

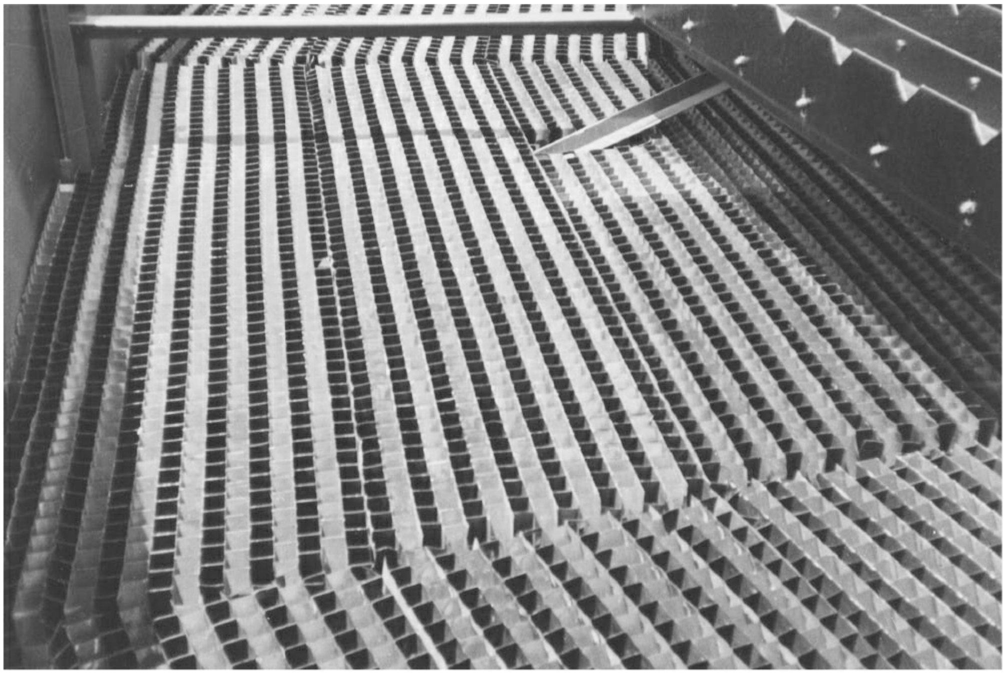


FIGURE 22.16 Plastic tube modules installed in an existing conventional clarifier. (*Courtesy of Neptune Microfloc, Inc.*)

Modules or packs of sloped parallel plates or tube settlers are used to increase the settling area of an existing conventional rectangular or circular clarifier (Fig. 22.16). The additional settling area increases the clarifier influent capacity, while the overflow rate either is reduced or remains constant. The modules are installed in the sedimentation zone of the clarifier and do not project into the clarifier's sludge thickening zone.

Actiflo® Clarifier

The Actiflo clarifier (Fig. 22.17) uses microsand as ballast to add weight to the floc for fast settling. The sand is added to a tank, where coagulant and effluent are added. The coagulation process occurs on the sand surface, and as the particles increase in size, their weight and settling rate are much higher than without the sand. The clarifier section of the unit is typically a lamella design with inclined plates. Since the rate of fall for the particle is much higher, the velocity of water (rise rate) can be much higher and still achieve excellent water clarity. These clarifiers are equipped with hydrocyclones to separate the microsand from the floc, so the sand can be reused. These clarifiers are often used for effluent treatment, where high flows are desired and physical space is limited. Typical rise rates range from 10 to 20 gpm/ft^2

($24–49\ m^3/[h \cdot m^2]$), and these rise rates are calculated based on the number of plates in the clarifier.

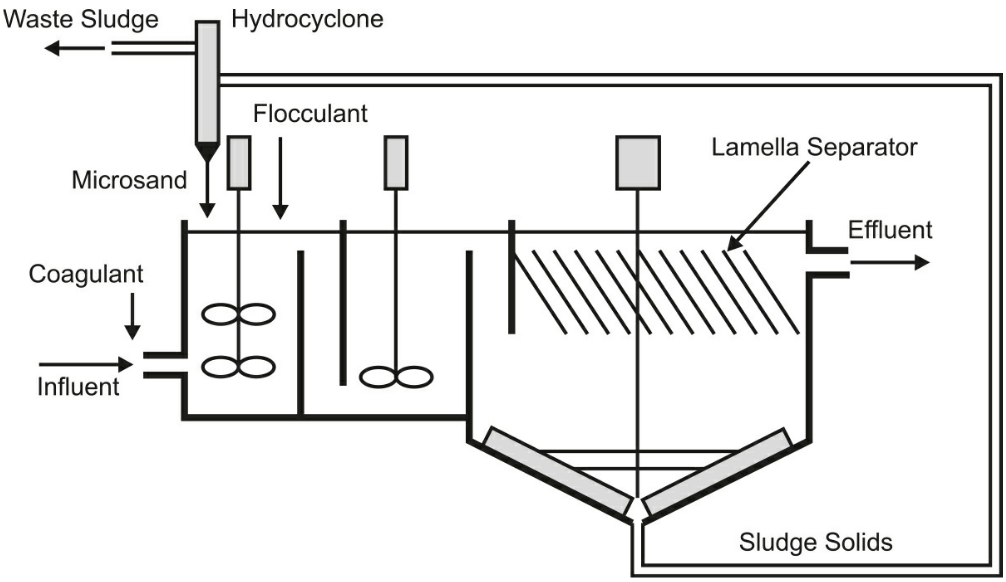


FIGURE 22.17 An illustration of an Actiflo® clarifier.

Densadeg® Clarifier

The Densadeg clarifier (Fig. 22.18) uses extensive mixing and solids contact to build heavy compact floc. There is a coagulation tank with fast mixing followed by a flocculation tank with relatively turbulent mixing. This flocculation tank circulates the water, which then flows up through a center cylinder, and then back down around the outside of the cylinder. Settled floc is returned to this tank to add solids and to increase solids contact. With the extensive mixing, the floc breaks down and reforms into more compact heavier floc. This process is quite compatible with lime softening and effluent treatment applications. The unit is somewhat more chemical demanding than the Actiflo unit, but it does not need microsand or hydrocyclones for operation. Typical rise rates range from 10 to 20 gpm/ft^2 ($24–49\ m^3/[h \cdot m^2]$).

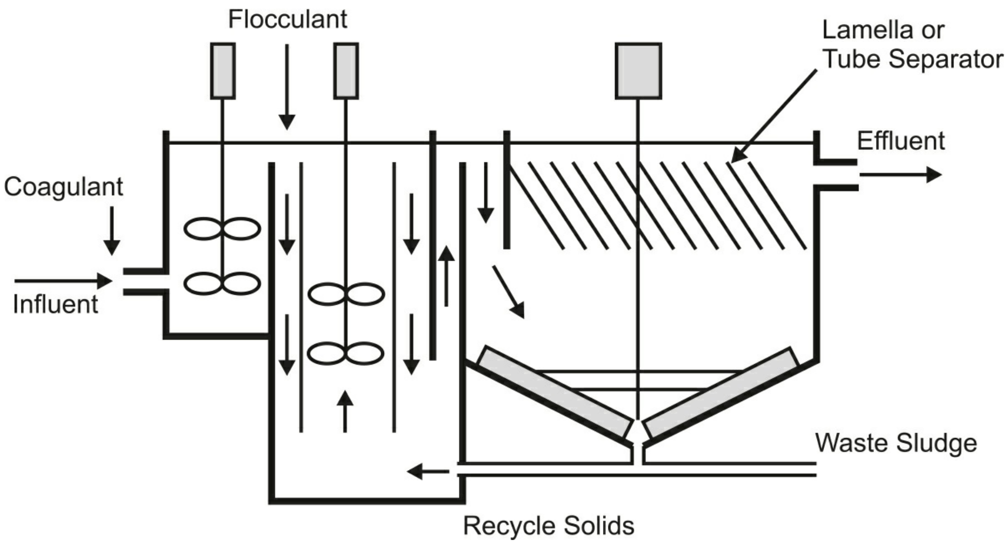


FIGURE 22.18 An illustration of a Densadeg® clarifier.

Drag Separator

The rectangular drag tank is a modification of the conventional rectangular clarifier constructed in either a concrete or steel basin. Figure 22.19 illustrates a concrete drag tank. The tank is designed for the removal of dense, anhydrous, gritty solids, such as granulated slag from a foundry cupola or hot strip steel mill scale. Water drains from the solids as they are dragged from the vessel by the flights moving up the beach. The movement of the flights up the beach breaks down fragile solids; hence, the type of solids in the effluent restricts drag tank applications. The detention time in the tank is usually short, limiting flocculation even when chemicals are used and resulting in poor effluent clarity. Chemical flocculation ahead of the tank improves effluent clarity. The flights can be arranged to skim the tank surface to remove floating material such as oil.

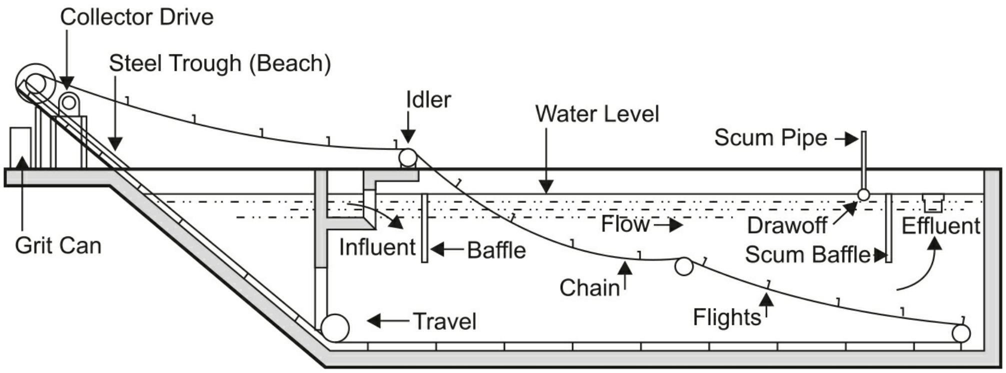


FIGURE 22.19 Drag tank. (*Courtesy of FMC Corporation*.)

Oil/Water Separators

An oil/water separator is used to separate free oil from effluents in refineries, chemical process plants, steel mills, and other industries as primary treatment. These units do not separate soluble impurities, nor do they break oil-in-water emulsions without chemical treatment. Settleable solids settle to the bottom of the basin or to a sludge collection pit. The types of oil/water separators include:

- American Petroleum Institute (API) separator
- Corrugated Plate Interceptor (CPI)
- Tilted Plate Interceptor (TPI) or Parallel Plate Interceptor (PPI)
- Circular oil/water separator

Generally, the free oil/water separator is the first unit in cleaning up an oily effluent before further treatment or reuse. In many cases, an equalization pond is located upstream from the separator. The pond equalizes the effluent flow and characteristics to the separator and through the effluent treatment system, to provide as constant as possible hydraulic and organic loadings on the separator and other processes. Wide variations in the flow to a separator affect the free oil capture efficiency, since the capture is directly related to the hydraulic loading. After the separator, the free oil ideally has been lowered to a level such that the remaining emulsified oil can be removed by DAF or similar device, to protect the following biological treatment process or meet oil discharge requirements.

API Separator

The API separator is a rectangular clarifier with chain and flight oil skimmers (Fig. 22.20), designed in accordance with procedures and specifications developed by the API. API has determined that the design of effluent separators should be based on the rate of rise of oil globules having diameters of 0.15 mm. This globule size, although somewhat arbitrary, has been adopted for design purposes. Both laboratory experiments and a study of existing plant data indicate that satisfactory free oil removal is achieved, when the 0.15 mm diameter particle is used.

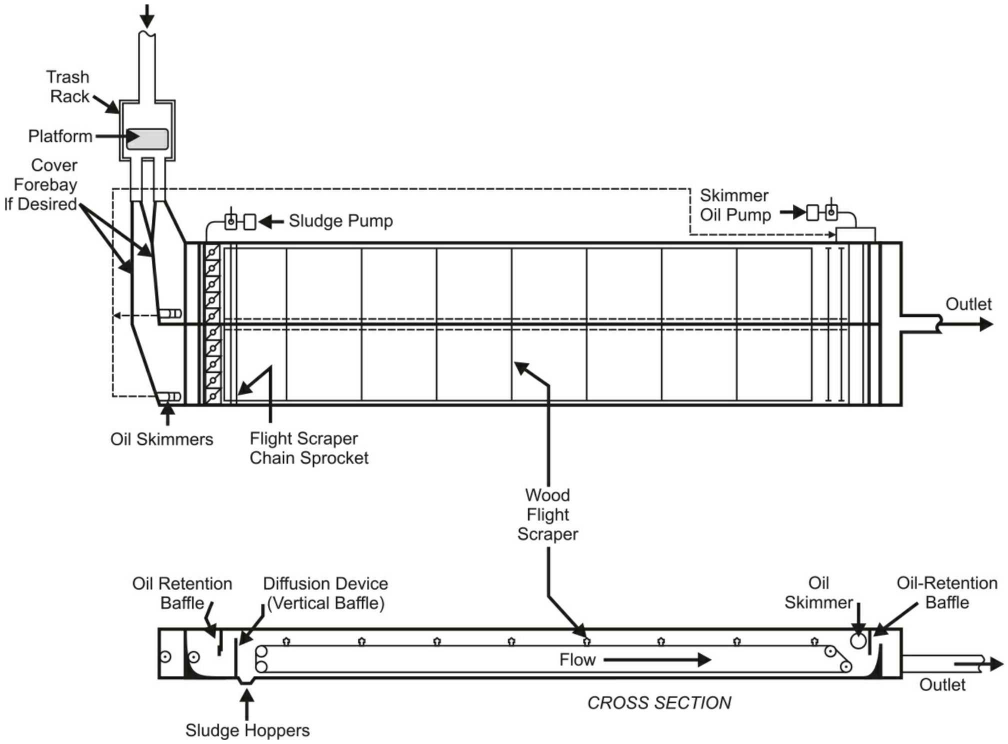


FIGURE 22.20 API separator.

The removal of a given oil globule is a function of the overflow rate (also called the rise rate) in an ideal separator, with no short-circuiting or turbulence. The overflow rate is the influent flow rate divided by the separator's surface area, and has the dimensions of velocity. Any oil globule with a rate of rise equal to or greater than the overflow rate is removed in the separator. This means that any globule having a rate of rise equal to or greater than the water depth divided by the retention time will reach the surface, even though it starts from the bottom of the basin.

The design of an API oil/water separator is based on four relationships:

1. The rise rate of 0.15 mm diameter oil globules is directly related to the difference in the specific gravity of the water and oil, and inversely to the absolute viscosity of the effluent at the design temperature.
2. The minimum horizontal area is based on the oil globule rise rate, corrected by the API factors for turbulence and short-circuiting in the separator.
3. A horizontal water flow not to exceed 15 times the oil globule rise rate or 3 ft/min (0.91 m/min).

4. A minimum water depth to separator width ratio of 0.3. The depth of the separator is to be 3 ft (0.91 m) minimum to 8 ft (2.4 m) maximum. The separator width limits are 6 ft (1.8 m) minimum to 20 ft (6.1 m) maximum. Chain and flight scrapers are limited to a maximum width of 20 ft (6.1 m).

The API standards further recommend, that a minimum of two parallel channels be provided, so that one is available for use when it becomes necessary for the other to be taken out of service for repair or cleaning.

A manually rotatable, slotted pipe skimmer is typically used for removal of the oil. Some installations use a rotating drum skimmer that can be either fixed or floating. The drum skimmer picks up a thin film of oil as it rotates, which is scraped off and drained into a collection sump. The drum can be made of carbon steel, stainless steel, aluminum, or plastic depending on the manufacturer. Optimum rotational speed is 0.5 to 1.5 ft/s (0.15–0.46 m/s) with a drum submergence of 0.5 inches (13 mm) or greater.

Corrugated Plate Interceptor

The CPI (Fig. 22.21) contains corrugated plates that are 0.75 to 2 inches (19–51 mm) apart, and at an angle of approximately 45° from vertical. Free oil globules rise only until contacting a corrugated plate, coalesce into larger drops with other globules, rise to the top of the plate pack, and finally to the water surface where they are skimmed off. The CPI maintains laminar flow conditions, while decreasing the distance that oil globules must rise to be collected, with an overall reduction of space taken by the oil/water separator. Settleable solids settle to the surface of the plates and drop down to the sludge pit.

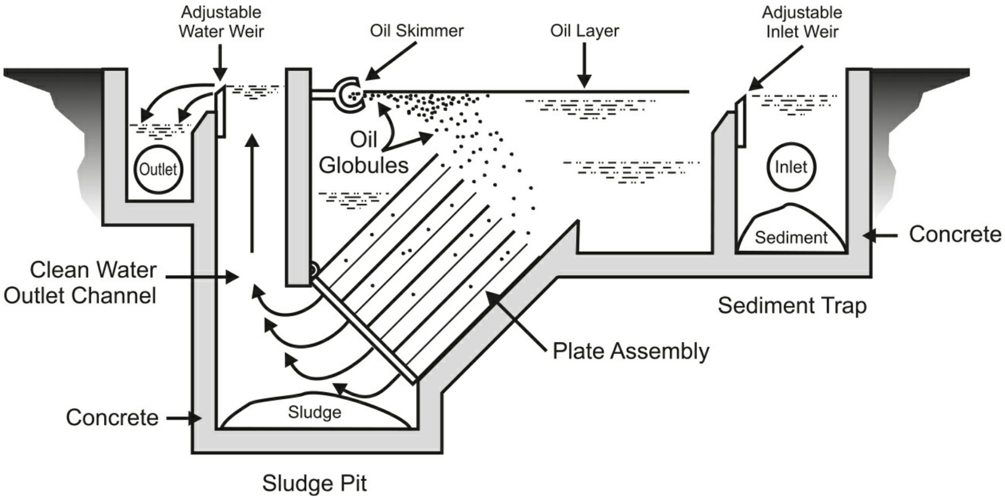


FIGURE 22.21 Corrugated plate interceptor.

The capacity of a CPI is based on the same free oil globule rise rate and hydraulic overflow principles as the API separator. In this case, the horizontal projected area of the corrugated plates, are used for the horizontal area in the API procedure.

Parallel Plate Interceptor

The PPI is similar to a plate clarifier. It is not extensively used in the refining or petrochemical industry, since the corrugated plates in the CPI are more efficient in coalescing free oil. However, PPI is used in other industries. The PPI operates on the same principles as the CPI.

Circular Oil/Water Separator

The design of circular oil/water separators follows the arrangement of conventional circular clarifiers with a central influent entrance, a discharge on the periphery, and includes sludge rakes and oil skimming. The sizing of the unit is the same as the API separator, since the circular arrangement provides a horizontal effluent flow, free oil globules rising, and suspended matter settling. A diagram of a circular oil/water separator is shown in Fig. 22.22. The larger clarifier handles the oily effluent, while the smaller is a primary clarifier for effluent that does not contain any oil.

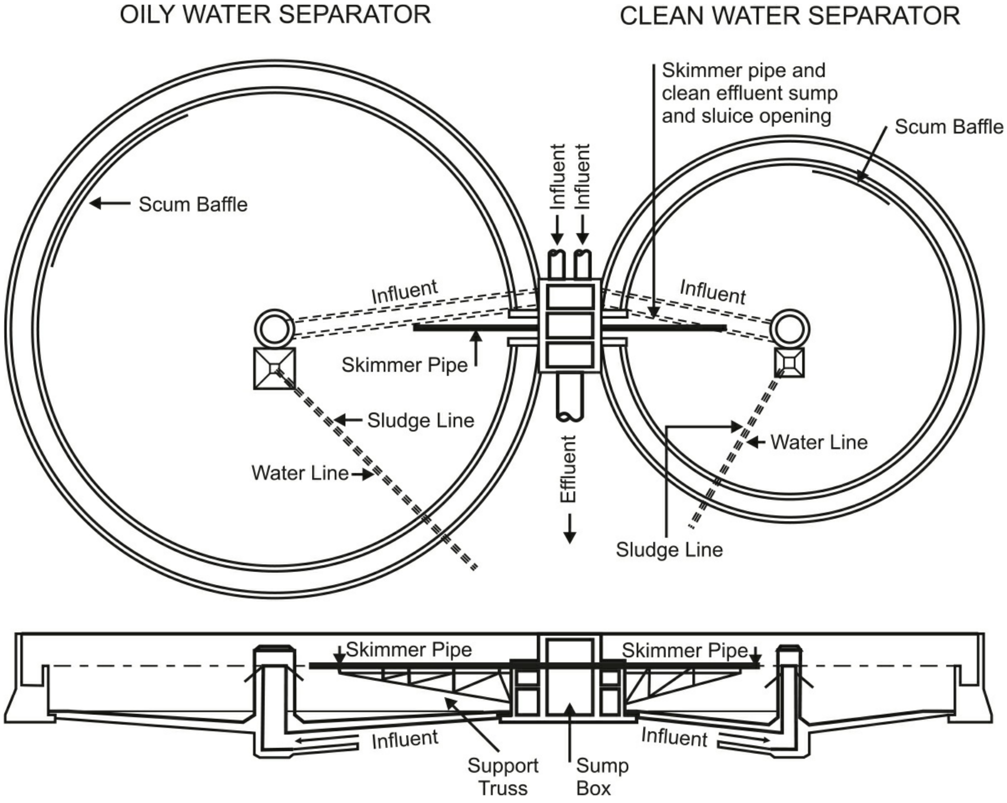


FIGURE 22.22 Circular oil/water separator.

Flotation Clarification

The DAF clarification process is used to separate suspended solids or liquors from water that are lighter than or only slightly heavier than water. These wastes include oils, fats, greases, fibers, biosolids (thickening and secondary clarification in biological treatment plants), algae, and metal hydroxides to name a few. DAF is therefore used in many industries such as oil refining, petrochemical, chemical, steel, meat and poultry packing, vegetable processing, pulp and paper, railroad terminals, and the prepared food industry. In these industries, oily waste may coat solid particles, giving them a tendency to float rather than settle. An API separator may precede the DAF system for the removal of free oil in many applications.

The flotation process consists of attaching fine gas bubbles (10–100 μm) to suspended solids or oily material, which reduces the specific gravity of the solids. The fine bubbles are produced by dissolving gas into the water at elevated pressure, followed by the subsequent reduction back to atmospheric pressure. The dissolved gas (in excess of atmospheric saturation) is released as fine bubbles, when the pressure is reduced. Air is commonly used as the gas, but other gases such as nitrogen are used, depending on the application. Nitrogen is used in applications where there is a possibility of explosion, such as refineries.

The Dissolved Air Flotation System

A schematic flow diagram of a typical DAF unit is illustrated in Fig. 22.23. Part of the effluent is saturated with air at the elevated pressure in the air saturation tank and recycled to the influent. The backpressure valve (also referred to as the pressure relief valve) at the indicated pressure release point in the flotation cell, reduces the pressure on the recycle flow where it mixes with the influent. The backpressure valve is located external to the flotation cell in other designs. In this case, the influent is mixed with the recycle flow after the pressure relief valve outside of the flotation cell. The excess dissolved air then comes out of solution, since the flow is now at atmospheric pressure, and the small gas bubbles attach to the particles in the effluent and rise to the surface of the cell. The floated material is skimmed off the cell for further handling or recovery. The clarified effluent is discharged, reclaimed, or receives further treatment, depending on discharge requirements. The flotation cell can be either circular or rectangular. The circular unit is more economical for larger flows.

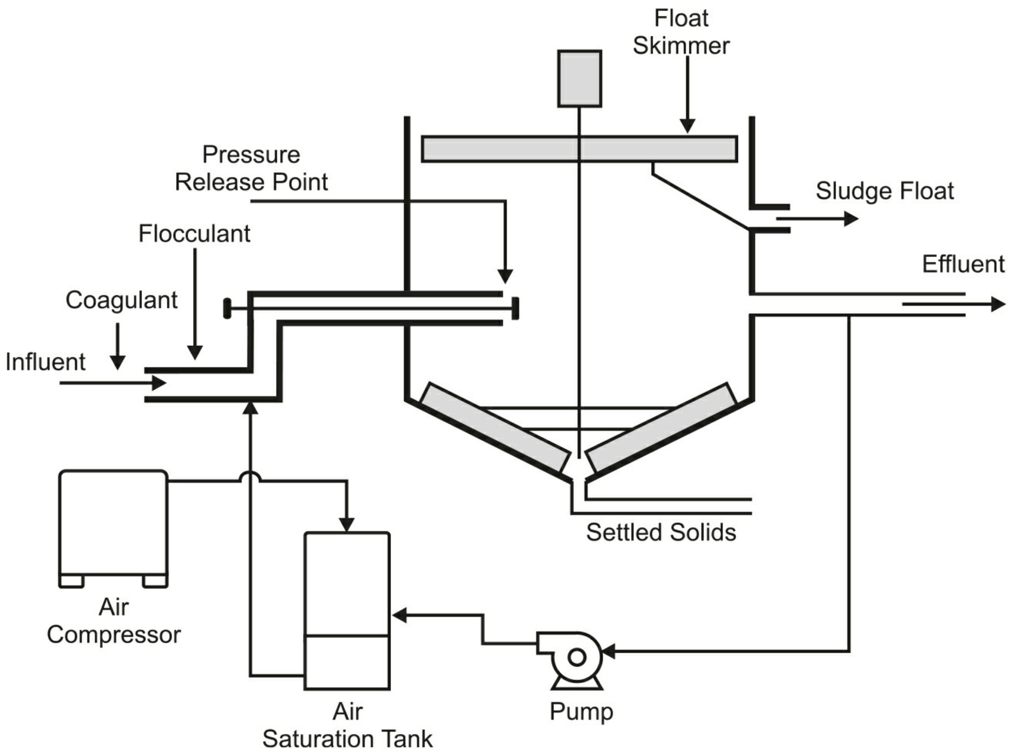


FIGURE 22.23 Dissolved air flotation system.

An organic flocculant or coagulant plus a flocculant are used in many instances to improve the solids capture or break oil emulsions. As in gravity settling, the coagulant can be an inorganic, such as an iron or aluminum salt, organic polymer, or a blend of inorganic and organic. Anionic, cationic, or nonionic organic flocculants may be used depending on the effluent. Cationic flocculants are most commonly used, since the small air bubbles have a slightly negative charge. A bench DAF column test (Fig. 22.24) can be used to simulate the clarification process and evaluate various chemical programs. The typical addition points for the chemicals are indicated in Fig. 22.23.

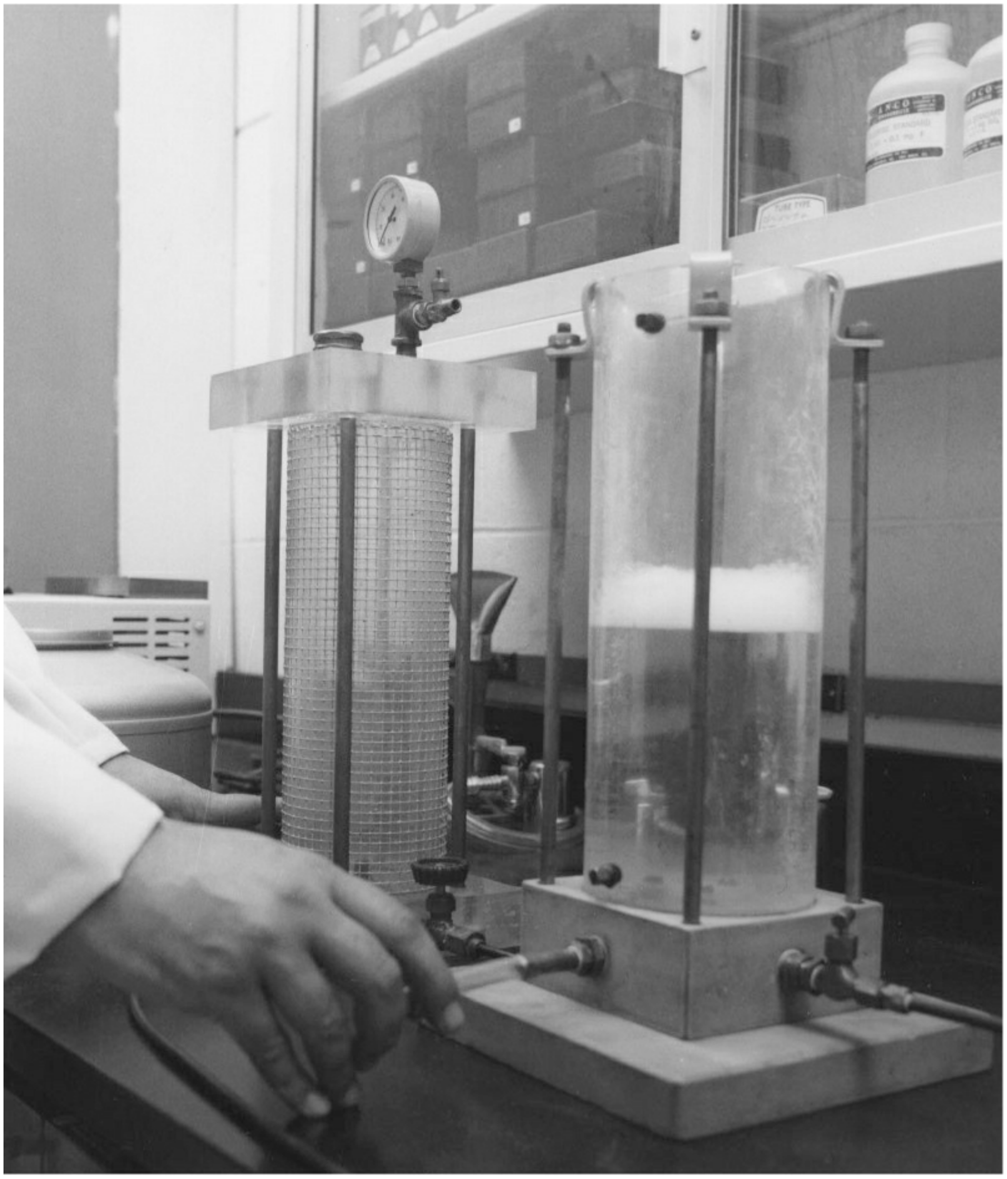


FIGURE 22.24 Bench DAF test. (*Courtesy of Infilco Degremont Inc.*)

Types of DAF Systems

The three different types of DAF systems are referred to as total pressurization, partial pressurization, and recycle pressurization. In total pressurization, the entire waste stream is pressurized and saturated with air (Fig. 22.25a). The material to be separated must be able to withstand the shearing forces in the pressure pump, air saturation tank, and backpressure valve, or the floc must be capable of quickly reforming after the pressure is released. In addition, the material in the effluent may plug the air saturation tank and backpressure valve, depending on the quantity and size of material.

This method is not used for oily or greasy wastes, as they can be mechanically emulsified.

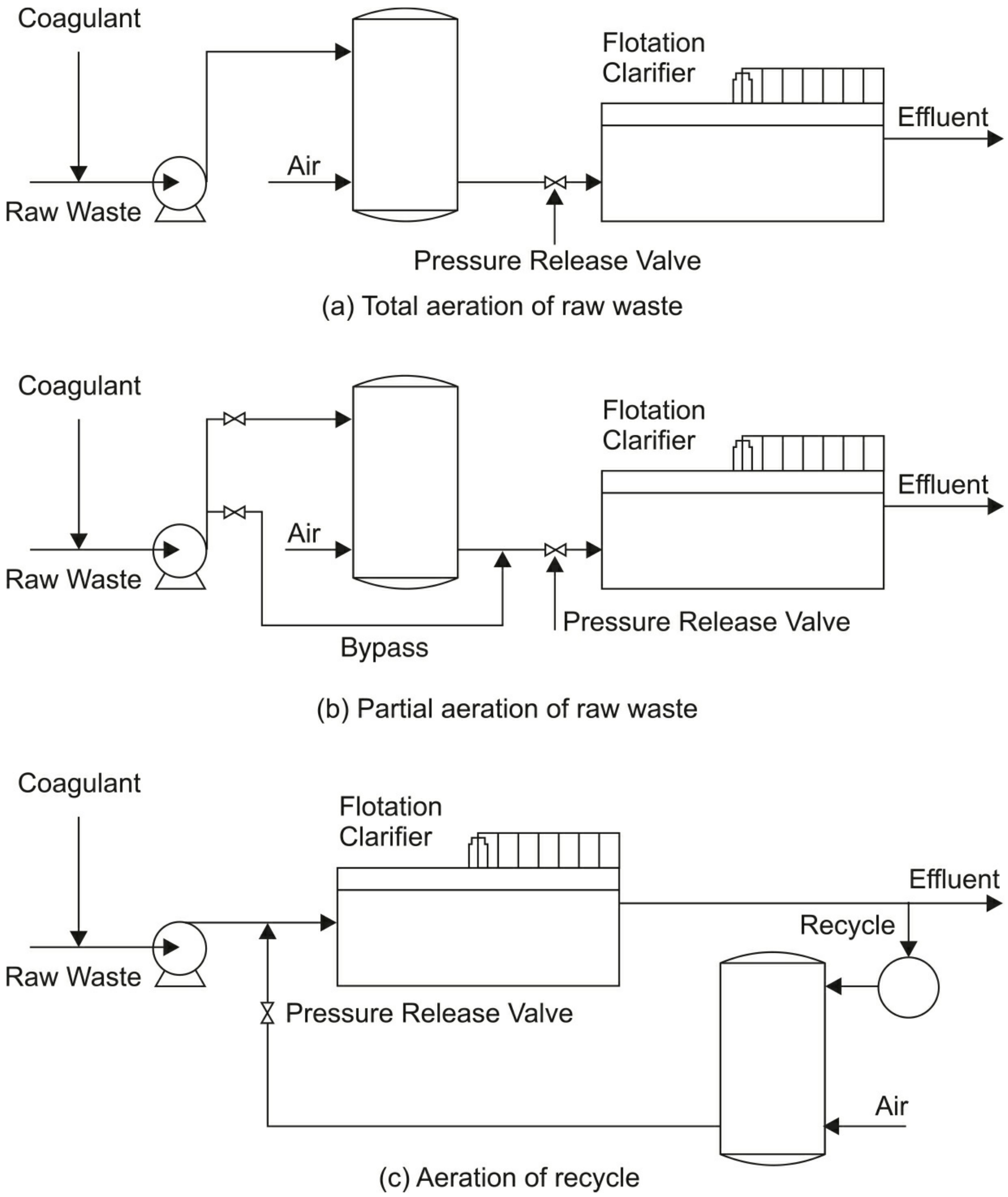


FIGURE 22.25 Types of DAF systems.

Only a portion of the influent is pressurized in partial pressurization (Fig. 22.25b). This method reduces pumping costs but has the same performance problems as indicated for total pressurization.

In recycle pressurization, (Fig. 22.25c) a side stream (recycled effluent) of clarified water is pressurized, saturated with air, and then mixed with the chemically pretreated waste stream. The pretreatment may be in a separate flocculation tank or in-line, depending on the application. This method is preferred when the effluent must be pretreated with chemicals, to eliminate shearing of the floc and eliminate plugging of the pressurization system. This is the preferred method to produce a low suspended solids effluent, even though the recycle flow increases the size of the flotation cell. Most systems today use recycled pressurization.

Operating Parameters

The hydraulic loading, expressed as gpm/ft^2 (m^3/[h · m^2]) of flotation area, typically controls the capacity of a DAF cell for clarification applications. The solids loading or flux, expressed as lb/[h · ft^2] (kg/[h · m^2]), may be the limiting factor, when the TSS are greater than about 1000 mg/L. The flotation effect is established by the recycle ratio and the air/solids ratio.

Hydraulic Loading Rate

The hydraulic loading rate (also referred to as rise rate or overflow rate) is one of the important considerations, since the degree of clarification efficiency is a function of the hydraulic loading. The loading rate is normally in the range of 1.5 to 2 gpm/ft^2 (3.7–4.9 m^3/[h · m^2]) including recycle. The higher loading is for "easy to float" material such as oil and grease, while the lower number is for "slow floating" material such as biosolids and algae. Generally, a rise rate greater than 2 gpm/ft^2 (4.9 m^3/[h · m^2]) results in higher effluent suspended solids. An exception is DAF systems floating fiber, such as white water clarification in paper mills, which are designed for 2.5 gpm/ft^2 (6.1 m^3/[h · m^2). These loading rates typically capture 80 to 85% of the suspended solids without chemical treatment, and 90 to 95% plus with chemical treatment. Chemical treatment is necessary to resolve oil and fat emulsions to obtain removal of these emulsified materials.

The hydraulic loading rate can be calculated using Eq. (22.5):

$$\mathrm{HLR} = \frac{(F_i + F_r)}{A} \tag{22.5}$$

where HLR = hydraulic loading rate, gpm/ft^2 (m^3/[h · m^2])
F_i = influent flow, gpm (m^3/h)
F_r = recycle flow, gpm (m^3/h)
A = net flotation area inside flotation baffles, ft^2 (m^2)

Some DAF cells have plate packs like parallel plate clarifiers to reduce the flotation cell floor space. The flotation cell hydraulic loading rate in this case is on the horizontal projected area of the plates, just like with plate clarifiers. The hydraulic loading rates previously discussed, are also used on the projected horizontal area in this case. Care must be taken to ensure that the loading rate is calculated on the floor space area and not the projected plate area.

Solids Loading Rate

The capacity for DAF clarification applications is typically controlled by the hydraulic loading rate. The solids loading rate determines the DAF capacity for clarification, when the influent solids exceed approximately 1000 mg/L and for biological solids thickening. Solids loading is calculated by dividing the influent TSS by the net flotation area. The solids in the recycle flow are customarily ignored in this calculation. The actual solids loading rate for clarification applications needs to be periodically checked using the following:

US Units

$$\mathrm{SLR} = \frac{(F_i)(\mathrm{TSS})}{(2000)(A)} \tag{22.6}$$

where SLR = solids loading rate, lb/[h · ft^2]
F_i = influent flow rate, gpm
TSS = total suspended solids, mg/L
A = net flotation area inside flotation baffles, ft^2

The 2000 factor = (694 gpm/mgd)(24 h/d)/8.33 lb/gal.

Metric Units

$$\text{SLR} = \frac{(F_i)(\text{TSS})}{(1000)(A)} \tag{22.7}$$

where SLR = solids loading rate, kg/[h · m^2]
F_i = influent flow rate, m^3/h
TSS = total suspended solids, mg/L
A = net flotation area inside flotation baffles, m^2
The 1000 factor = (10^6 mg/kg)(1 m^3/1000 L).

Typical solids loading rates are 1.5 lb/[h · ft^2] (7.3 kg/[h · m^2]) without chemicals and 2 lb/[h · ft^2] (9.8 kg/[h · m^2]) with chemical treatment. A polymer can be used to increase the solids loading rate to achieve the same solids capture or improve the solids capture efficiency at lower loading rate.

Air/Solids Ratio

The performance of a flotation system depends on having sufficient air bubbles present to make contact with the suspended solids and float them. An insufficient quantity of air results in only partial flotation and poor clarification. On the other hand, excessive amounts of air can cause turbulence and high surface velocity, which can lead to short-circuiting and high effluent suspended solids. The performance of a flotation unit in terms of effluent quality and float solids concentration is related to an air/solids ratio, defined as pound (kilogram) air per pound (kilogram) dry suspended solids. The ratio is calculated from operating data using Eq. (22.8):

$$A/S = \frac{1.3(\text{Air})(\text{ERT})(F_r)}{(\text{TSS})(F)} \tag{22.8}$$

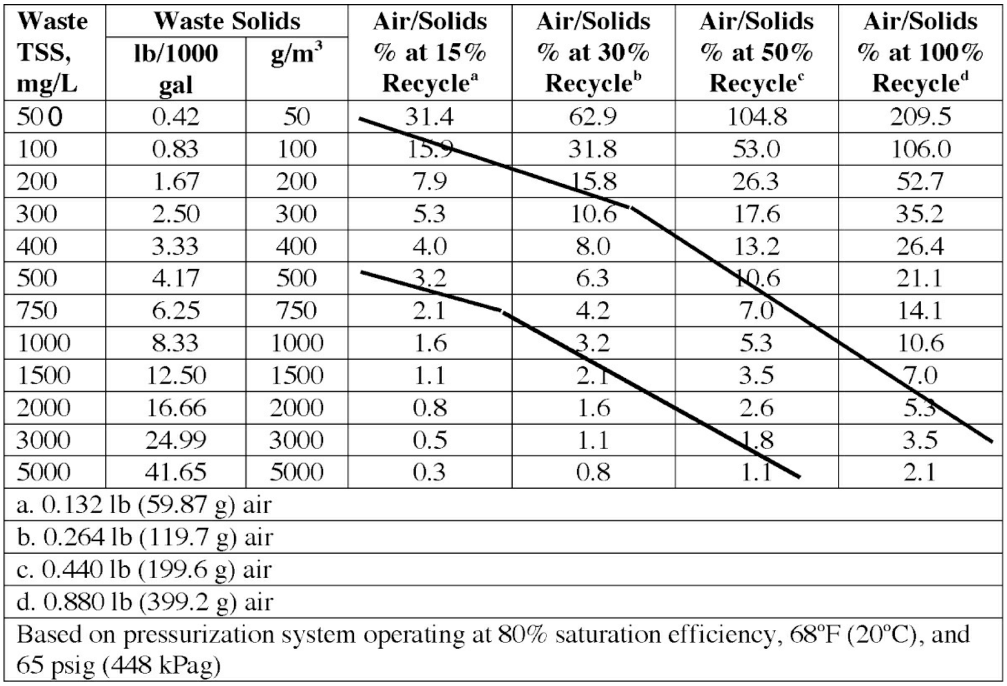
where A/S = air/solids ratio, lb/lb (kg/kg)
Air = air solubility at operating conditions, mL/L
ERT = saturation tank (pressurization tank) efficiency, decimal
F_r = recycle flow rate, gpm (m^3/h)
TSS = total influent suspended solids, mg/L
F = influent flow rate, gpm (m^3/h)
1.3 = approximates the density of air at ambient temperature, mg/cm^3

The air saturation tank dissolving efficiency (ERT) is in the range of 0.5 to 0.8 for clean water depending on the manufacturer.

Recycle Ratio

In DAF clarification, the term recycle, expressed in percent of total influent flow, has been historically used instead of the air/solids ratio, even though the air/solids ratio is critical to the clarification process. Normally, the necessary air/solids ratio in clarification processes is considerably higher that what is used in DAF thickening. The main consideration in clarification is to provide a sufficient quantity of air bubbles to find and contact the suspended solids. Statistically, more air bubbles are needed to contact the considerably lower influent suspended solids concentration in clarification of dilute suspensions, as opposed to thickening applications. This low influent suspended solids concentration is the reason for the higher air/solids ratio.

Figure 22.26 gives a general picture of the recycle rate requirement, based on the TSS in the effluent. This figure was compiled from several DAF units treating a variety of effluents including oil, fiber, fat, grease, latex, and others in a diversity of industries. The area between the operational range lines gives a choice of two recycle rates; the lower recycle rate is selected for an “easy to float” material, and the higher rate for a “slow floating material.” A recycle rate of 30 to 50% is generally used, if the influent TSS are unknown, depending on how hard or easy the material is to float.



Waste TSS, mg/L	Waste Solids		Air/Solids % at 15% Recycle[a]	Air/Solids % at 30% Recycle[b]	Air/Solids % at 50% Recycle[c]	Air/Solids % at 100% Recycle[d]
	lb/1000 gal	g/m³				
500	0.42	50	31.4	62.9	104.8	209.5
100	0.83	100	15.9	31.8	53.0	106.0
200	1.67	200	7.9	15.8	26.3	52.7
300	2.50	300	5.3	10.6	17.6	35.2
400	3.33	400	4.0	8.0	13.2	26.4
500	4.17	500	3.2	6.3	10.6	21.1
750	6.25	750	2.1	4.2	7.0	14.1
1000	8.33	1000	1.6	3.2	5.3	10.6
1500	12.50	1500	1.1	2.1	3.5	7.0
2000	16.66	2000	0.8	1.6	2.6	5.3
3000	24.99	3000	0.5	1.1	1.8	3.5
5000	41.65	5000	0.3	0.8	1.1	2.1

a. 0.132 lb (59.87 g) air

b. 0.264 lb (119.7 g) air

c. 0.440 lb (199.6 g) air

d. 0.880 lb (399.2 g) air

Based on pressurization system operating at 80% saturation efficiency, 68°F (20°C), and 65 psig (448 kPag)

FIGURE 22.26 Suggested recycle rates for DAF clarification process based on waste TSS.

Generally, effluents containing oils, fats, greases, fibers, and other lighter than water solids are classified as easy to float. Types of slow floating materials are biosolids, metal hydroxides, algae, and granular media solids.

Pressurization Systems

Figure 22.27 is a diagram of a typical pressurization system for a DAF system. The operating pressure of the system just upstream from the pressure relief (backpressure) valve is generally 60 to 70 psig (414–483 kPag), although there are a few manufactures that design their systems for 40 to 45 psig (276–310 kPag). The system should be operated at the manufacture's design operating pressure, as any changes in pressure result in changes in recycle flow, hydraulic loading, saturation tank retention time, air dissolving efficiency, and quantity of air dissolved.

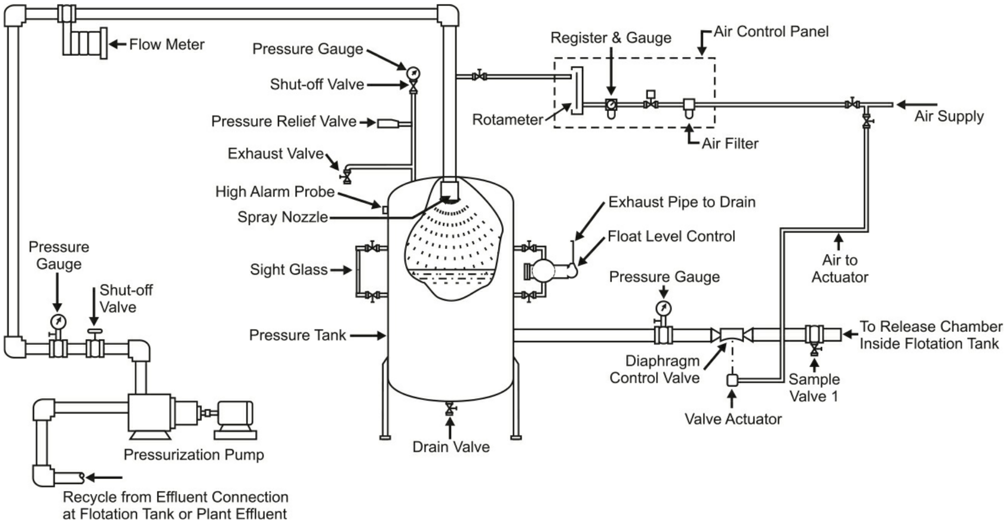


FIGURE 22.27 Typical pressurization system.

The internals of the saturation tank are designed to break the recycle water into small droplets, to maximize the water surface area and thus the transfer rate of the gas into the liquid. The internals vary depending on the manufacturer, and can be spray nozzles (Fig. 22.28), packing similar to a high-rate cooling tower, spray jet with a splash plate, and various baffle configurations. All of these designs require a gas atmosphere above the liquid level in the tank.

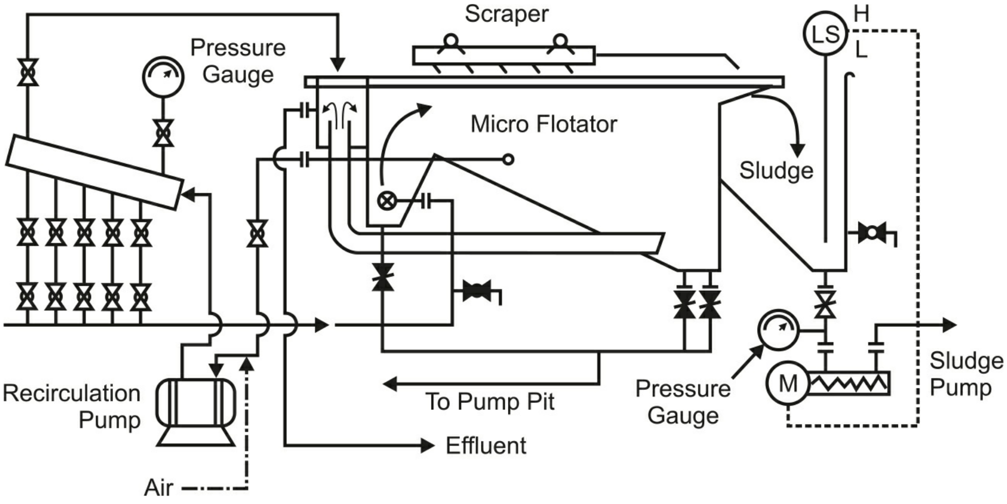


FIGURE 22.28 DAF system without air saturation tank.

The liquid level in the saturation tank is controlled in one of two ways. The first, referred to as the bleed-off system, continuously feeds air to the tank. A level control valve (Fig. 22.29) opens with decreasing water surface, to vent air that has not gone into solution, and returns the water surface to its design elevation. The second is called the on/off feed air system in that the air to the tank is turned on/off in response to the rising/falling of the water surface in the tank.

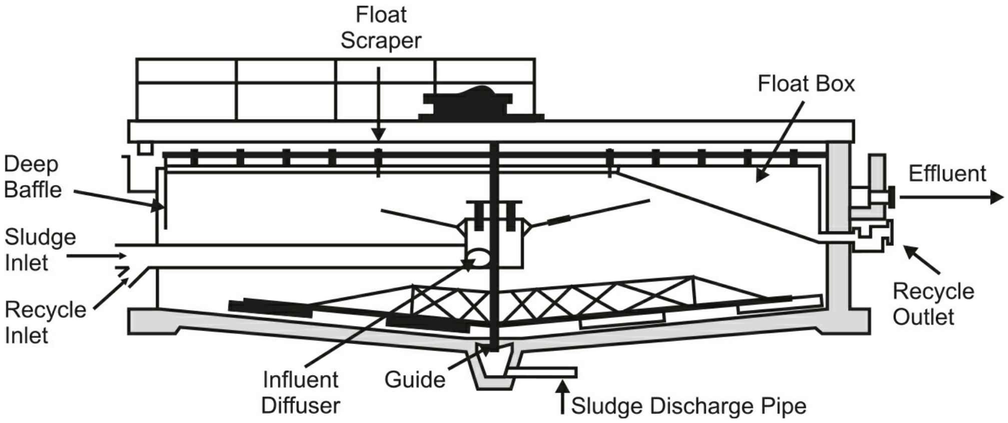


FIGURE 22.29 Circular flotation cell.

Losing the water level surface control by flooding the tank with air or water, due to too much or too little air addition, or failure of the automatic level control system, are common causes for failure of the flotation process. Flooding the tank with air results in poor dissolving efficiency and the presence of "geyser" eruptions on the surface of the flotation cell, due to the free air being introduced into the cell. Flooding the tank with water results in the destruction of the water droplet production in the tank and the loss of air dissolving efficiency.

Some DAF designs do not use an air saturation tank (Fig. 22.28). Instead, a centrifugal pump that is specially designed to handle air-in-water solutions is used. The pump is capable of handling up to 35% entrained air without air binding, and produces air bubbles down to 30 µm. The design in Fig. 22.28 uses a slanted tube to vent excess air and several backpressure valves to release the system pressure. This type of system is used in easier to float applications, such as poultry packing effluent.

A milky white water in the flotation cell indicates that the pressurization system is functioning properly. High dissolved solids or antifoams in the effluent can adversely affect air solubility, reducing the amount of small air bubbles available for flotation.

Flotation Cell

The circular flotation cell or tank is similar to a circular clarifier having surface skimmers and sludge rakes or plows (Fig. 22.29). The number of skimmers provided is based on the anticipated float quantity. The influent is introduced at about mid-depth in a horizontal direction to prevent the flow from boiling in the center of the tank. A deep flotation baffle is provided around the periphery, so that the clarified water must flow downward from the inlet to the effluent weirs, while the floating material rises.

Another type of circular flotation cell is called the shallow tank configuration (Fig. 22.30), since the side water depth of the tank is only about 2.5 ft (0.76 m), while the more conventional circular cell (Fig. 22.29) has a tank side water depth of 6 to 8 ft (1.8–2.4 m). The influent feed containing the recycle flow, is introduced into the tank from a rotating, radial manifold. The rotational velocity of the manifold is opposite to, and set equal to, the influent water velocity. The influent is thus introduced into the tank at essentially zero velocity. This in essence static condition allows efficient flotation in the shallow tank, leaving the clarified water in the lower stratum of the tank, from where it is removed by the effluent extraction pipes attached to the rotating carriage. The rotating scoop attached to the carriage lifts the floated solids from the surface and transports them to the center of the unit, from where they are discharged from the tank. This type of unit is commonly used in the pulp and paper industry.

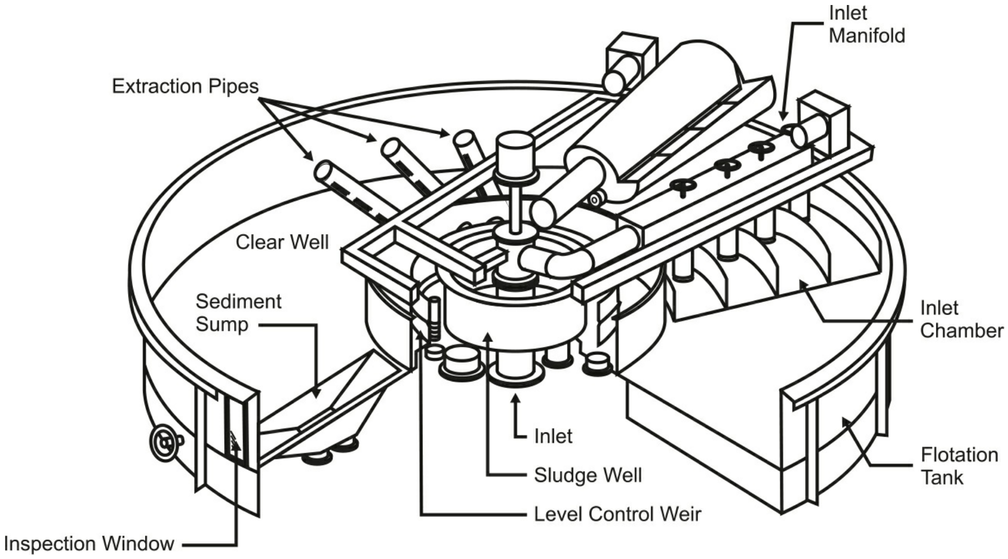


FIGURE 22.30 Shallow tank flotation cell.

A rectangular flotation cell may be equipped with a chain and flight scraper for the floated material, and a second chain and flight scraper for the settled sludge (Fig. 22.31). Depending on the application, only a scraper for the float may be provided, in which case the floor of the basin may be sloped to hoppers. A reciprocating float scraper mechanism in place of the chain and flight type is used in some designs. The float is scraped to a sump at the feed end of the basin. An adjustable effluent overflow weir is provided, following a deep float containment baffle.

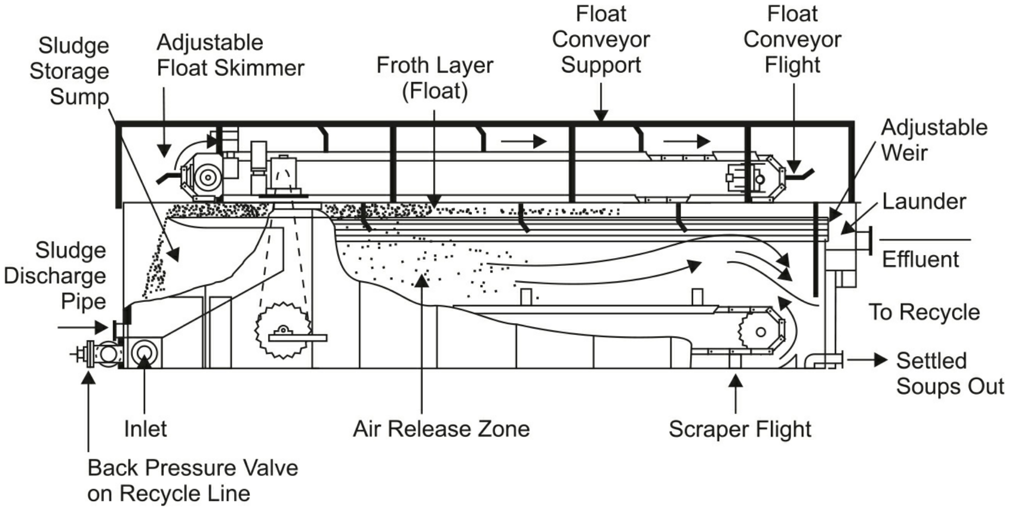


FIGURE 22.31 Rectangular flotation cell.

Float Removal Control

Most DAF units are equipped with adjustable overflow effluent weirs that determine the operating water level in the unit. Consequently, the weirs control how deep or shallow the skimmer blades dip into the floated solids. The water level rises as the overflow weir is raised, permitting the skimmer blades to dip more deeply into the floated material. This results in a greater percent of the floated material being removed with each pass of the skimmer. This in turn normally results in a cleaner effluent but a wetter (lower percent solids) float. Lowering the weir has the opposite effect. The solids get dryer (higher percent solids), but the effluent quality may deteriorate.

Float skimmer blades remove the floated material from the top of the flotation unit. The skimmers may be driven by variable speed motors, which operate continuously, or by constant speed motors, operating intermittently on a timer. In either case, the mechanism needs to be adjusted to remove the float at the rate dictated by the treatment goals.

Generally, the slower (run less frequently) the skimmers move, the drier the float removed, but deterioration of the effluent water quality may result. Increasing the speed of the skimmers (run more frequently) results in more total solids being removed, which may improve the effluent quality at the expense of a wetter float.

Plant Flows

Minimum, maximum, and average flows must be considered and provisions made to cope with surges. A DAF clarifier is hydraulically capable of processing a higher flow rate with a constant recycle rate for brief or infrequent surges in plant flow, but the effluent quality may suffer. An equalization basin ahead of the DAF system is best for eliminating large, regular variations in effluent, so that the system can be operated at as constant a flow as possible. Generally, reducing overflow rates below 1 $\mathrm{gpm/ft^2}$ (2.4 $\mathrm{m^3/[h \cdot m^2]}$) does not measurably improve suspended solids capture.

Induced Air Flotation (IAF)

Mechanically entraining air and dispersing it through the liquid as fine bubbles, in contrast to the release of dissolved gas from solution, is also used to achieve flotation. A rectangular tank is divided into four flotation cells. Each cell is equipped with either a motor-driven aerating rotor mechanism, or an aspirating nozzle. (Fig. 22.32 illustrates the nozzle arrangement.) The specially designed rotor mechanism or nozzle draws air into the cell and disperses it throughout the cell. Oil globules and fine suspended solids attach to the bubbles as they rise to the surface, from where they are removed by skimmer paddles.

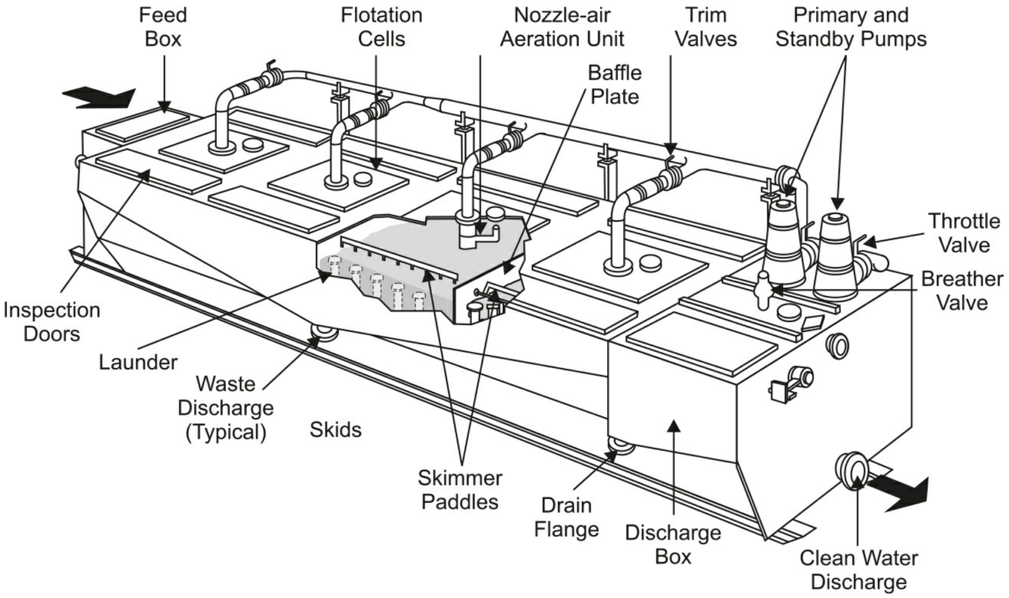


FIGURE 22.32 Nozzle-type-induced air flotation. (*Courtesy of Wemco Division, Envirotech Corporation*.)

The induced air flotation system is primarily used to remove oil from effluents with or without the addition of chemicals. It cannot handle effluents that contain heavy, settleable solids that will not float, since the unit does not have any capabilities for removing settled sludge.

CHAPTER 23

Secondary Effluent Treatment

Secondary effluent treatment systems are biological systems with the purpose of processing primary effluent system effluent. The main goal of secondary effluent treatment is to remove soluble pollutants from effluent. During secondary effluent treatment, consideration must be given to handling of sludge, where microbial organisms under proper environmental conditions perform an effluent decontamination function. Descriptions of the major types of secondary effluent processes are presented, accompanied by equations for the chemistry involved and information on equipment design and performance parameters.

General Principles of Secondary Treatment

Secondary treatment processes in the overall waste treatment system have three major purposes:

1. Biological oxidization of soluble organic matter that remains after primary treatment
2. Absorption of suspended solids carried over from primary treatment as well as settling of solids generated as a result of the biological process
3. Biological removal of certain nutrients like ammonia, nitrate, and phosphorus that are dissolved in effluent

Secondary biological treatment requires availability of many microorganisms (bacteria), good contact between these organisms and organic material, availability of oxygen, sufficient nutrients, favorable temperature conditions, favorable pH ranges, and adequate time for organisms to work.

Microorganisms in secondary treatment systems need a source of food or energy [biochemical oxygen demand (BOD)], time (the biological process retention time), and a source of oxygen to function effectively and efficiently.

Secondary or biological waste treatment processes can be classified by the presence or absence of dissolved oxygen (DO). Terms usually applied to this classification are:

- Aerobic—Usually DO is maintained higher than 0.5 mg/L. Optimum is 1–2 mg/L or slightly higher in specific cases.
- Anoxic—DO should be less than 0.5 mg/L and most preferably nondetectable. Combined oxygen such as nitrate and nitrite can be presented.
- Anaerobic—DO should be nondetectable and no nitrate or nitrite source exists.

Biological treatment processes can also be classified according to their means of providing medium for the biological organisms growth:

- Attached growth—a mass of individual microorganisms attaching themselves to a fixed media (e.g., plastic rings) in a slime film (sometimes called fixed film)
- Suspended or slurry growth—a process where microorganisms are kept in a suspended state, as individual organisms, or as a mass of organisms (sludge flocs) that are mixed with the effluent being treated in a solids suspension termed mixed liquor

In modern waste treatment facility designs, there are usually two common components of a typical waste treatment system:

1. A biological reactor or vessel, in which effluent comes in contact with the microbial population
2. A clarifier, in which biological solids are settled and collected in the sludge blanket and thereby separated from clarified effluent, which passes to the receiving waters

Table 23.1 shows the major biological treatment processes used for different treatment.

Type	Common Name	Use*
Aerobic Processes		
Suspended growth	Activated sludge:	
	Conventional (plug flow) Continuous flow stirred tank Step aeration Pure oxygen Modified aeration Contact stabilization Extended aeration Oxidation ditch	Carbonaceous BOD removal (nitrification)
	Suspended growth nitrification	Nitrification
	Aerated lagoon	Carbonaceous BOD removal (nitrification)
	Aerobic digestion:	
	Conventional air	Stabilization
	Pure oxygen	Carbonaceous BOD removal
	High-rate aerobic algal pond	Carbonaceous BOD removal
Attached growth	Trickling filter:	
	Low rate High rate	Carbonaceous BOD removal (nitrification)
	Roughing filter	Carbonaceous BOD removal
	Rotating biological contactor (RBC)	Carbonaceous BOD removal (nitrification)
	Packed bed reactor	Nitrification
Combined processes	Trickling filter, activated sludge Activated sludge, trickling filter	Carbonaceous BOD removal (nitrification)
Anoxic Processes		
Suspended growth	Denitrification	Denitrification
Attached growth	Denitrification	Denitrification

Suspended growth	Anaerobic digestion:	
	Standard rate single stage High rate single stage Two stage	Stabilization, carbonaceous BOD removal
	Anaerobic contact process	Carbonaceous BOD removal
Attached growth	Anaerobic filter	Carbonaceous BOD removal, stabilization (denitrification)
	Anaerobic lagoon (pond)	Carbonaceous BOD removal, stabilization
Aerobic/Anoxic or Anaerobic Processes		
Suspended growth	Single stage	Carbonaceous BOD removal, nitrification, denitrification
Attached growth	Nitrification/denitrification	Nitrification/denitrification
Combined processes	Facultative lagoon (pond)	Carbonaceous BOD removal
	Maturation or tertiary pond	Carbonaceous BOD removal (nitrification)
	Anaerobic-facultative lagoon	Carbonaceous BOD removal
	Anaerobic-facultative-aerobic lagoon	Carbonaceous BOD removal

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*Major use is presented first; other uses are shown in parentheses.

TABLE 23.1 Major Biological Processes Used for Effluent Treatment

Basic Methods of Secondary Treatment

Secondary effluent treatment methods include activated sludge, aerated lagoons, trickling filters, and rotating biological contactors.

Activated Sludge

The activated sludge process is a suspended growth biological effluent treatment technique, in which a mixture of effluent and biological mass (microorganisms) is agitated and aerated. The biological mass is subsequently separated from treated effluent in a clarifier, and returned to the aeration process to maintain a balance of biological solids and effluent being treated. The activated sludge process derives its name from the biological mass formed when air is continuously injected into nutrient-rich effluent. Microorganisms are mixed thoroughly with organics under conditions that stimulate use of organics as a food source. As microorganisms grow, multiply, and mix by agitation with air, individual organisms clump together (flocculate), to form an active mass of microbes called activated sludge. Variations of the activated sludge process are discussed in a later section.

Aerated Lagoon

An aerated lagoon is a basin in which effluent is treated on a flow-through basis. Oxygen is usually supplied by surface aerators or submerged aeration devices.

Trickling Filter

The trickling filter process is a fixed-film biological process that uses slag, rock, stones, plastic, or wood as medium on which microorganisms grow. Effluent is typically applied as a spray from moving distributors. As effluent trickles through the bed, microorganisms grow on the surface of the packing in a fixed film. Effluent passes over and through the medium to provide needed contact between microorganisms and organics. Biological growth sloughs off the medium when the inner biological area can no longer receive oxygen. A clarifier is used after the trickling filter to remove this biological material before discharging treated water. Sometimes, effluent from the clarifier is recycled back to the trickling filter to increase BOD removal efficiency, and maintain optimum hydraulic loading on the filter.

Rotating Biological Contactor

This process is a fixed-film biological process that uses rotating discs mounted on shafts and placed in a tank, with about 40% of the disc area immersed in the tank (effluent) and the remainder exposed to the atmosphere. A biological film or biomass grows on the surface of the discs. Rotation brings biomass in contact with effluent for removal of organics and with the atmosphere for absorption of oxygen. A secondary clarifier collects excess solids that are produced on the biodiscs.

Principles of Biological Waste Treatment

In the biological treatment of effluents, a mixed population of microorganisms uses colloidal and dissolved organics found in effluent from primary treatment as its main food supply. In consuming these organics, microorganisms use part of the organic substances to obtain energy needed for their life activities.

Biological respiration, in the presence of DO, produces products such as carbon dioxide, water, sulfates, nitrates, and phosphates. The remaining part of consumed organics is used as building blocks in a series of synthesis (reproduction) reactions, which result in an increased microorganism population (cell growth). Therefore, colloidal and dissolved organics originally present in effluent are transformed partly into a stable form, such as carbon dioxide, and partly into a viable biological mass. This biochemical reaction is active in all biological treatment processes.

The biological mass is subsequently separated from the effluent in secondary clarifiers, to ensure a proper degree of treatment within effluent and water quality standards.

Important Microorganisms

In the activated sludge process, microorganisms are dispersed throughout the water phase; in trickling filters, RBCs, and other fixed-film processes, microorganisms are attached to a fixed surface, forming a biological film. In either process, microorganisms are doing the work, and therefore, all precautions must be taken to assure a favorable environment for them.

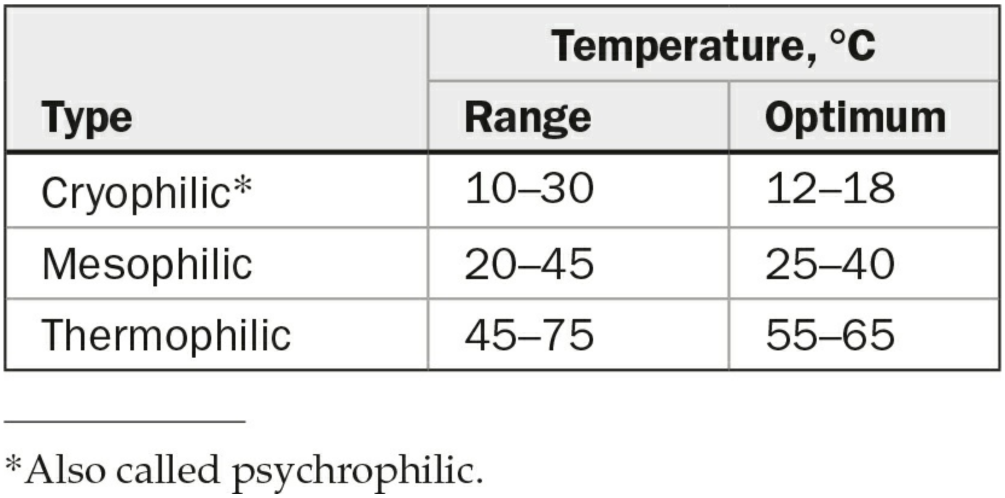
Microorganisms considered important in biological treatment are: bacteria, fungi, algae, protozoa, rotifers, and worms.

Bacteria

Bacteria are single-cell microorganisms. They use soluble food and, in general, are found wherever moisture and a food source are available. Their usual mode of reproduction is by binary fission (i.e., by dividing, the original cell becomes two new organisms), although some species reproduce sexually or by budding. Even though there are thousands of different species of bacteria, their general form falls into one of three categories: spherical, cylindrical, and helical. Bacteria vary widely in size. Representative sizes are 0.5 to 1.0 μm in diameter for the spherical, 0.5 to 1.0 μm in width by 1.5 to 3.0 μm in length for the cylindrical (rods), and 0.5 to 5 μm in width by 6 to 15 μm in length for the helical (spiral).

In general, two types of bacteria can be distinguished: floc forming and filament forming. Floc-forming bacteria have the capability, under the right conditions, to clump together using excreted exocellular polymer to form a floc that is large and heavy enough to settle. Filament-forming bacteria also remove organics from effluent but are characterized by stringy or threadlike forms that are extremely light and easily washed out from the clarifier. It is clear that floc formers are preferred in a biological treatment plant. The character and type of effluent as well as the environment (regime in which they live) dictate which forms will be the majority.

Temperature and pH play a vital role in the life and death of bacteria. The rate of reaction for microorganisms increases with increasing temperature, doubling with about every 18°F (10°C) of temperature rise, until some limiting temperature is reached. According to the temperature range in which they function best, bacteria may be classified as cryophilic (psychrophilic), mesophilic, or thermophilic. Typical temperature ranges for bacteria in each of these categories are presented in Table 23.2.



	Temperature, °C	
Type	**Range**	**Optimum**
Cryophilic*	10–30	12–18
Mesophilic	20–45	25–40
Thermophilic	45–75	55–65

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*Also called psychrophilic.

TABLE 23.2 Typical Temperature Ranges for Various Bacteria

The vast majority of secondary treatment plants is designed for mesophilic organisms and needs to be operated in the 25 to 40°C range for best treatment.

The pH of a solution is also a key factor in the growth of organisms. Most organisms cannot tolerate pH levels above 9.5 or below 4.0. Generally, optimum pH for bacteria growth lies between 6.5 and 7.5.

Fungi

In biological treatment systems, fungi are considered multicellular, nonphotosynthetic, and heterotrophic organisms.

Most fungi are strict aerobes. They have the ability to grow under low moisture conditions and can tolerate an environment with relatively low pH. Optimum pH for most species is 5.6; the range is 2 to 9. Fungi have a low nitrogen requirement, needing only approximately one-half as much as bacteria.

The ability of fungi to survive under low pH and nitrogen conditions makes them very important in the biological treatment of some industrial wastes.

Algae

Algae are unicellular or multicellular, autotrophic, and photosynthetic organisms. In oxidation ponds, algae are valuable in that they have the ability to produce oxygen through photosynthesis. At night, when light is no longer available for photosynthesis, algae consume oxygen in respiration, producing carbon dioxide (CO_2). Oxygen is also consumed by biological decomposition of dead algae. (High die off of algae results in stagnant ponds with their associated odors.) Respiration also occurs in the presence of sunlight; however, the net reaction is production of oxygen. Equations 23.1 and 23.2 represent simplified biochemical reactions for photosynthesis and respiration:

Photosynthesis:

$$CO_2 + 2H_2O + \text{light} \rightarrow CH_2O + O_2 + H_2O \tag{23.1}$$

CH_2O represents new algae cells.

Respiration:

$$CH_2O + O_2 \rightarrow CO_2 + H_2O \tag{23.2}$$

In an aquatic environment, it can be seen that this type of metabolic system produces a diurnal variation in DO. The ability of algae to produce oxygen is vital to the ecology of the water environment. In some types of biological treatment (oxidation pond), algae are needed to supply oxygen to aerobic, heterotrophic bacteria.

Algae are also considered a nuisance in waste treatment. Algae cells may form large floating mats that reduce the oxygen transfer ability of a treatment tank or clog filters. The die off of large quantities of algae at night depletes DO, and the pond becomes odorous due to anaerobic decomposition of dead algae. They also cause an increase in effluent total suspended solids (TSS) levels from lagoon systems or activated sludge clarifiers, particularly during summer months.

Protozoa

Protozoa are motile, microscopic organisms that are usually single cells. The majority of protozoa are aerobic heterotrophs, although a few are anaerobic. Protozoa are generally an order of magnitude larger than bacteria and often consume bacteria as an energy source. In effect, protozoa act as polishers of effluents from biological waste treatment processes by consuming free swimming bacteria and particulate organic matter.

Ciliata Movement by means of cilia is characteristic of these protozoa. Cilia are hair-like extensions from the cell membrane. Besides being responsible for movement, they are also important in assisting protozoa to capture solid food. Sanitary engineers usually consider *Ciliata* to be divided into two types: free-swimming and stalked. The free-swimming type must swim after bacteria. They require a great deal of food, because they expend so much energy in swimming. *Paramecium* is a free-swimming ciliate that is important in effluent treatment. Stalked ciliates may be attached to something solid and must catch food as it passes. Because their movement is limited or free-floating, they require less food for energy. *Vorticella* is a stalked ciliate that is important in biological treatment processes, especially in the activated sludge process.

Rotifers

The rotifer is an aerobic, heterotrophic, multicellular organism. Its name is derived from the fact that it has two sets of rotating cilia on its head, which are used for motility and capturing food. Rotifers are very effective in consuming dispersed and flocculated bacteria and small particles of organic matter. Their presence in mixed liquor indicates a highly efficient aerobic biological purification process.

Worms

Worms are characteristic higher life forms that appear in activated sludge systems with very high sludge age.

Bacterial Growth

Bacteria generally reproduce by binary fission. The time required for each fission, which is termed the generation time, can vary from days to less than 20 minutes. The general growth pattern of bacteria in a batch culture is shown in Fig. 23.1. Initially, a small number of organisms are inoculated into a culture medium, and the number of viable organisms is recorded as a function of time. The growth pattern based on the number of cells has four more or less distinct phases:

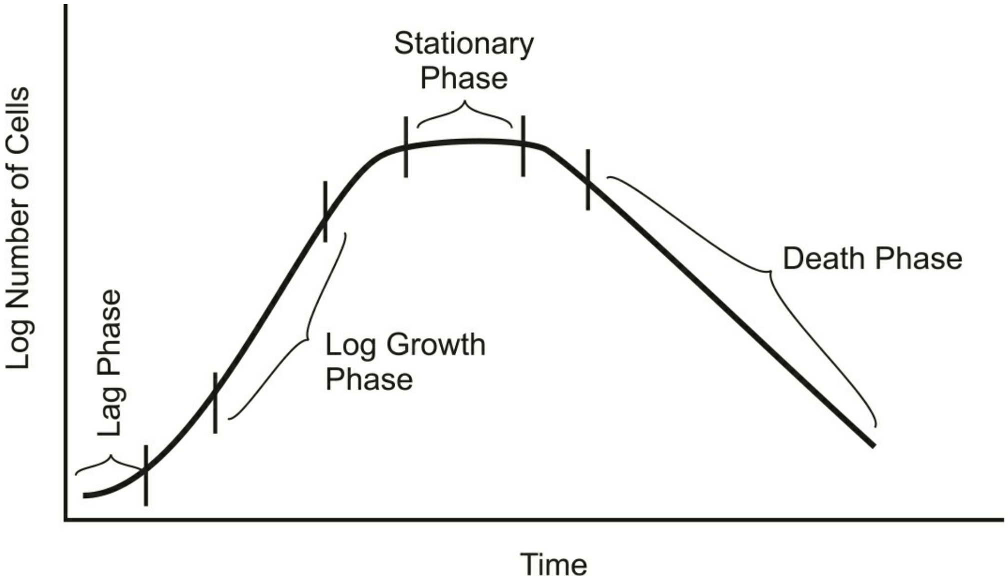

FIGURE 23.1 Typical bacteria growth curve.

1. Lag Phase—Upon addition of an inoculum to a culture medium, the lag phase represents the time required for organisms to acclimate to their new environment.
2. Log Growth Phase—During this period, cells divide at a rate determined by their generation time and their ability to process food (constant percentage growth rate).
3. Stationary Phase—Here, the population remains stationary. Stationary growth occurs because cells have exhausted substrate or nutrients necessary for growth, and growth of new cells is offset by death of old cells.
4. Log Death Phase—During this phase, the bacterial death rate exceeds production of new cells. The death rate is usually a function of the

viable population and environmental characteristics. In some cases, the log death phase is the inverse of the log growth phase.

The growth pattern is described in terms of the variation of the mass of microorganisms with time. This growth pattern consists of the following four phases:

1. Log Growth Phase—There is always an excess amount of food surrounding the microorganisms, and the rate of metabolism and growth is related to the ability of the microorganism to consume food.
2. Stationary Phase—The availability of food and the microorganisms are in balance.
3. Declining Growth Phase—The rate of growth and hence the mass of bacteria decrease because of limitations in the food supply.
4. Endogenous Phase—Microorganisms are forced to metabolize their own protoplasm without replacement because the concentration of available food is at a minimum. During this phase, a phenomenon known as lysis can occur, in which nutrients remaining in dead cells diffuse out to furnish remaining live cells with food.

It is important to note that the preceding discussions concerned a single population of microorganisms. Biological treatment units are composed of complex, interrelated, mixed biological populations, with each particular microorganism in the system having its own growth curve. The position and shape of a particular growth curve in the system, on a time scale, depends on food and nutrients available and environmental factors such as temperature, pH, and whether the system is aerobic or anaerobic.

Bacterial Oxidation

As previously discussed, secondary treatment or the conversion of organic matter to stable end products is accomplished aerobically, anaerobically, or facultatively (alternating presence and absence of oxygen), using suspended growth or attached growth systems. A portion of organic material is oxidized to obtain energy necessary for synthesis of new cell mass. As organics are removed, microorganism cell matter is metabolized to stable end products. In most biological treatment systems, these processes occur simultaneously.

The three processes may be represented as follows for an aerobic process:

1. Oxidation:

$$\begin{aligned}&\text{Organic matter (COHNS)} + O_2 + \text{bacteria} \rightarrow \\ &\quad CO_2 + H_2O + \text{other energy end products}\end{aligned} \tag{23.3}$$

2. Synthesis:

$$\begin{aligned}&\text{Organic matter (COHNS)} + O_2 + \text{bacteria} + \text{energy} \rightarrow \\ &\quad C_5H_7NO_2 \ \text{(new bacterial cells)}\end{aligned} \tag{23.4}$$

3. Endogenous respiration:

$$C_5H_7NO_2 + 5O_2 \rightarrow 5CO_2 + NH_3 + 2H_2O + \text{energy} \tag{23.5}$$

In these equations, COHNS represents organic matter in effluent. The formula $C_5H_7NO_2$, which represents bacteria cells, is a generalized value obtained from experimental studies. Although the endogenous respiration reaction is shown as resulting in relatively simple end products and energy, stable organic end products are also formed.

Biological Treatment Control Parameters

To ensure a favorable environment to promote the reactions involved in the biological treatment process, the following parameters must be controlled:

- pH and alkalinity
- Temperature
- Oxygen requirements
- Nutrient requirements
- Solids separation
- Biological solids recirculation
- Aeration capacity
- Mixing energy

- Hydraulic retention time
- Solids retention time

Biological waste treatment removes organic matter in effluent in much the same manner as naturally occurring stream biota would in surface receiving waters. However, there is usually not as much time to break down solid organic matter in biological treatment. Generally, microorganisms in biological waste treatment work most efficiently on dissolved organic matter. These active microorganisms are a relatively small fraction of the total biological process biomass. Certain constituents adversely affect the biological treatment process. Major constituents and their effects on the biological treatment process are shown in Table 23.3.

Constituent	**Condition***
Ammonia nitrogen	Needed for growth; too low a level can inhibit growth; high levels of unionized ammonia can inhibit nitrification.
Phosphate	Needed for growth; too low a level can inhibit growth.
Calcium and magnesium	Very small amounts needed for growth.
Chloride	Corrosive; toxic to microorganisms at very high levels.
Mercury	Toxic to microorganisms at designated levels.
Other heavy metals	Toxic to microorganisms at designated levels.
Sulfate	Needed in small amounts.
Sulfide	Corrosive; depletes oxygen; toxic for nitrification bacteria.
Petrochemicals	Toxic to microorganisms at high levels.
Phenol compounds	Toxic to microorganisms at high levels until organisms acclimate.
Surfactants	Cause foaming and can decrease oxygen transfer efficiency.

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*Toxicity levels are dependent upon average and peak loadings.

TABLE 23.3 Biological Treatment System’s Critical Constituents

Certain substances present in municipal and industrial effluents are more biodegradable than others. A relative comparison of biodegradability of various constituents commonly found in effluent is shown in Table 23.4.

Easily Biodegradable	Slower or Moderately Biodegradable			Less Easily Biodegradable
Sugars Alcohols	Ketones Phenol compounds	Organic acids	Esters Ethers	Cellulose Fats Lignins Polymeric compounds Hydrocarbons: Aliphatic Aromatic Alkyl, aryl Chlorinated aromatics

TABLE 23.4 Relative Biodegradability of Organic Compounds

pH and Alkalinity

pH of effluent is not always a problem. However, in biological treatment, pH can drop mainly because of nitrate and carbon dioxide generation from BOD and nitrogen. Operation of most biological processes is limited to a pH range of 5 to 9 (optimum is 6.5–7.5). If effluent does not contain enough alkalinity (bicarbonate), biological production of carbon dioxide and nitrate can drop pH out of the optimum range. If pH drops below the optimum range, caustics, limes, or other alkalis can be added as needed.

Alkalinity is the measured capacity of a solution's ability to react with acid [usually sulfuric acid (H_2SO_4)] to a predetermined pH such as 4.2. The higher the alkalinity, the higher the demands for the neutralizing agent (or acid) for a pH drop. Therefore, pH does not drop much even with carbon dioxide and nitrate formation when effluent alkalinity is high.

Systems designed for nitrification and denitrification require pH between 7.2 and 8.0. At pH above or below this level, nitrification may slow down. At $pH < 6$, nitrification completely stops.

Temperature

Temperature affects all biological processes. Biological oxidation rates increase to a maximum at about 95°F (35°C) for most treatment systems. At temperatures greater than 95°F (35°C), treatment efficiency decreases by reducing bacterial floc formation. Temperatures in excess of 99°F (37°C) show a definite effect on biological systems. It is possible, however, in certain wastes, to operate efficiently at somewhat higher temperatures. Lower temperatures than 50°F (10°C) also affect performance of biological processes, especially nitrification efficiency.

The rate of biological activity is influenced by temperature because of the depth of penetration of oxygen into the floc or film. Oxygen penetration increases as temperature decreases, since oxygen is not used as quickly at floc surfaces and greater numbers of organisms per unit surface can react. Oxygen solubility also increases as temperature decreases.

Sludge Production

Sludge production in a biological treatment system is expressed as the net effect of the following two processes:

1. Synthesis of new organisms resulting from assimilation of organic matter removed
2. Reduction of the mass of organisms under aeration by the process of die off and oxidation over an extended period (known as endogenous respiration)

Figure 23.2 shows the pathway of carbon contained in effluent.

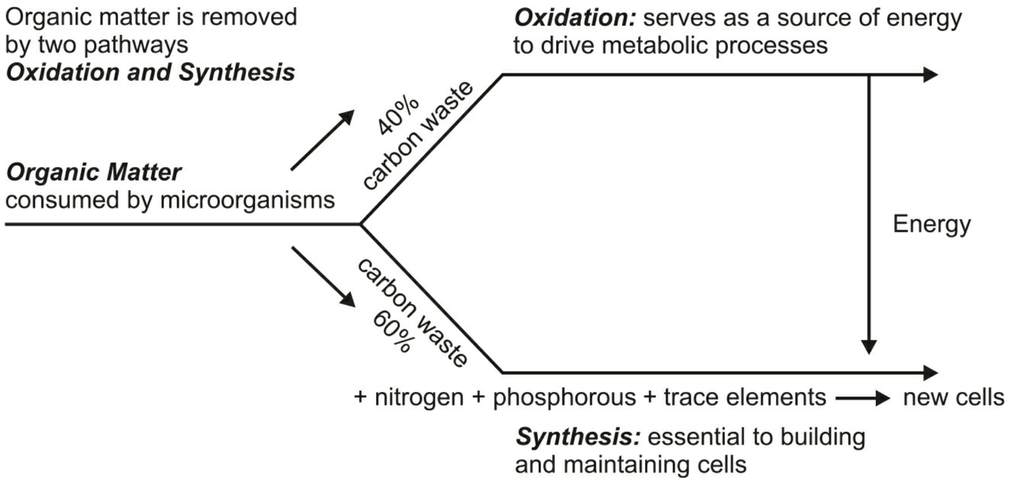

FIGURE 23.2 Carbon pathways in effluent.

As a result, net sludge production is mainly functions of total BOD treated in the process and solids retention time (SRT), which is also known as mean cell residence time (MCRT). For the activated sludge process where SRT is 5 to 10 days, sludge yield is typically 0.5 to 0.6 lb as dry mass when 1 lb of domestic BOD (0.5–0.6 kg/kg) is treated, and lower with longer SRT. Sludge yield is different for different types of industrial effluents.

Oxygen Requirements

Theoretical oxygen requirements can be determined from the five-day BOD (BOD_5) of effluent, less the amount of organisms wasted from the system per day. If all of the BOD_5 were converted to end products (CO_2 and H_2O), total oxygen demand would be computed by converting the BOD_5 to BOD_L (all carbonaceous BOD converted to end products), using an appropriate conversion factor. A portion of the waste is converted to cell structure, and is removed from the system, however. Therefore, if BOD_L of the wasted cells is subtracted from the total, the remaining amount represents the amount of oxygen that must be supplied to the system. It is known that one mole of cells is equal to 1.42 times the concentration of cells [Eq. (23.6)]. The theoretical oxygen requirements for removal of carbonaceous organic matter in effluent by an activated sludge system are:

$$\mathrm{OD}_C = [Q(S' - S)f_C/f_{\mathrm{BOD}}] - 1.42P_x \tag{23.6}$$

where OD_C = carbonaceous oxygen demand, lb O_2/d (kg O_2/d)
Q = influent effluent flow rate, mgd (m^3/d)
S' = influent BOD, mg/L
S = effluent BOD, mg/L
f_C = unit conversion factor, 8.34 lb/gal for US units [(1000 L/m^3) (1 kg/10^6 mg) = 1/1000 for metric units]
f_{BOD} = conversion factor for converting BOD_5 to BOD_L, dimensionless (0.68 for municipal effluent)
P_x = net sludge production in terms of volatile solids, lb/d (kg/d)

When nitrification occurs, the total oxygen requirement is that required for removal of carbonaceous organic matter [Eq. (23.6)], plus oxygen required for conversion of ammonia to nitrate as follows:

$$\mathrm{OD}_N = 4.57Q(N_0 - N)f_C \quad (23.7)$$

where OD_N = nitrification oxygen demand, lb O_2/d (kg O_2/d)
Q = influent effluent flow rate, mgd (m^3/d)
N_0 = influent total Kjeldahl nitrogen (TKN), mg/L
N = effluent total Kjeldahl nitrogen (TKN), mg/L
4.57 = conversion factor for amount of oxygen needed for complete oxidation of TKN
f_C = unit conversion factor, 8.34 lb/gal for US units [(1000 L/m^3) (1 kg/10^6 mg) = 1/1000 for metric units]

Based on the oxygen requirement, the aeration rate is calculated considering oxygen transfer efficiency, and the oxygen content in air using the Eq. (23.8). Oxygen transfer efficiency depends on mixed liquor suspended solids (MLSS) in the aeration basin, diffuser type, temperature, basin depth, residual DO, etc. In an aeration basin having a depth of 15 ft (4.6 m), overall oxygen transfer efficiency is typically 8 to 12% with coarse bubble air diffusers. Fine bubble diffuser efficiency is in the range of 20 to 30%. Many plants have converted from coarse to fine bubbles to save energy.

$$\mathrm{AR} = \mathrm{O}/[4(\varepsilon)(d)] \quad (23.8)$$

where AR = aeration rate, m^3 air/min (1 m^3 = 35.3 ft^3)
O = oxygen requirement, kg O_2/d
ε = specific oxygen transfer efficiency, /m (commonly 0.015–0.03/m)
d = aeration basin depth, m

A very rough rule-of-thumb for the total amount of oxygen that should be supplied to a biological effluent treatment plant is approximately 2 to 4 lb O_2/lb BOD removed (2–4 kg/kg) for low loaded systems [0.05 lb BOD/lb MLSS (0.05 kg/kg)], and 1.5 to 2.5 lb O_2/lb BOD removed (1.5–2.5 kg/kg) for medium loaded systems [0.1–0.2 lb BOD/lb MLSS (0.1–0.2 kg/kg)].

Nutrient Requirements

In general, a ratio of BOD/nitrogen/phosphorus of 100/5/1 is recommended for maintaining the best biological conditions. For healthy growth, it is important to have sufficient nutrients by maintaining a small excess in the final effluent. Approximately 1 or 2 mg/L nitrogen [as ammonia (NH_3)] and soluble orthophosphate (filtered sample) in the effluent is sufficient. Phosphoric acid and mono, di, and trisodium phosphate are used as sources of phosphorous. Polyphosphates and hexametaphosphate are not a readily available source of phosphate for microorganisms, and should not be used. Anhydrous or aqueous ammonia and urea are used as sources of nitrogen. Ammonium phosphate can also be used, but it is difficult to meet the different demands for nitrogen and phosphorus additions.

In addition to nitrogen and phosphorous, many other mineral elements are essential for proper metabolic activity of microorganisms involved in waste treatment. Table 23.5 summarizes minimum nutrient requirements for effluent having a BOD of 200 mg/L. At higher BOD, minimum requirements of the nutrients increase proportionally.

Element	Bacterial Composition, mg/g biomass COD*	Minimum Influent Concentration, mg/L
N	87	10
P	17	2
K	10	1.2
Ca	10	1.2
Mg	7	0.8
S	6	0.7
Na	3	0.4
Cl	3	0.4
Fe	2	0.2
Zn	0.2	0.02
Mn	0.1	0.01

*Chemical oxygen demand.

TABLE 23.5 Typical Substrate and Nutrient Requirements for Effluent with 200 mg/L BOD (300 mg/L COD)

Municipal effluents usually contain enough of all micronutrients. However, many industrial effluents suffer from nutrient deficiency due to a narrow range of raw materials. For example, effluents in the chemical and pharmaceutical industries often contain low levels of mineral elements, while organic contents represented by BOD and chemical oxygen demand (COD) are very high. For proper biological treatment, micronutrients such as K, Ca, Mg, S, and Fe should be added as needed along with N and P.

Solids Separation

One of the most important aspects of biological waste treatment is in the design of facilities used to separate biological solids from treated effluent. Secondary sedimentation must perform two functions:

1. Separate MLSS from treated effluent
2. Thicken return sludge and waste activated sludge

Both functions are affected by surface area and depth of the sedimentation basin. Ample volume must be provided for storage of solids during periods in which sustained peak plant loadings are experienced. In addition, peak daily flow rate variations must be considered because they affect sludge removal requirements. The secondary clarifier/thickener must be sized for either the hydraulic loading (gpd/ft^2 or m^3/[h · m^2]), or solids flux (lb solids/[d · ft^2] or kg/[h · m^2]). In most cases, solids flux or loading is the critical parameter.

Return Sludge Requirements

The purpose of the return of settled solids is to maintain a sufficient concentration of activated sludge in the aeration tank, so that the required degree of treatment can be obtained in the time interval desired. Return of activated sludge from the clarifier to the inlet of the aeration tank is essential to the process.

Solids tend to form a sludge blanket in the bottom of the clarifier/thicker, which varies in thickness from time to time. If solids thickening capacity of the secondary clarifier is inadequate, solids may fill the entire depth of the tank at peak flows. Return sludge pump capacities vary between 25 and over 200% of influent flow, depending upon operational strategy and condition.

Activated Sludge Process

The activated sludge process was developed in England in 1914, and was so named because it involves production of an active mass of microorganisms capable of stabilizing organic content of waste in the presence of DO. Activated sludge is probably the most versatile of biological treatment processes. The process has found wide application in both domestic and industrial effluent treatment.

Activated sludge is a biological contact process where bacteria, protozoa, and small organisms such as rotifers are commonly found. Bacteria are the most important group of microorganisms, because they are responsible for the structural and functional activity of the activated sludge floc. All types of bacteria (except pathogens) make up activated sludge. The predominant type is determined by the nature of organic substances in effluent, mode of operation of the plant, and environmental conditions present for organisms in the process.

The conventional activated sludge process consists of an aeration tank, secondary clarifier, method of returning sludge to the aeration tank, and means of wasting excess sludge from the system (see Fig. 23.3). Sludge wasting is accomplished from the recycle or mixed liquor line. The flow model is plug flow with clarifier underflow recycle. Both influent settled effluent, and recycled sludge enter the tank at the head end, and are aerated for a period of 4 to 12 hours. Influent effluent and recycled sludge are mixed by the action of diffused or mechanical aeration, which is constant in a well-operated system as mixed liquor moves down the tank.

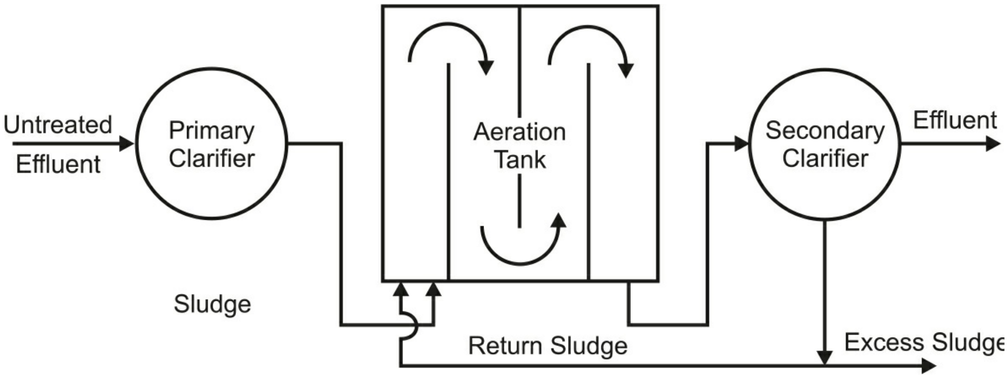

FIGURE 23.3 Conventional plug flow activated sludge process.

During this period, absorption, flocculation, and oxidation of organic matter occur. Mixed liquor is settled in the activated sludge clarifier/thickener, and sludge is returned at a rate of approximately 25 to 100% of the influent flow rate.

Activated Sludge Process Equipment

All activated sludge processes have certain process equipment similarities. These are discussed in the following paragraphs.

Aeration Tanks

Aeration tanks used in activated sludge processes are usually constructed of reinforced concrete and left open to the atmosphere. A cross section of a typical aeration tank is shown in Fig. 23.4.

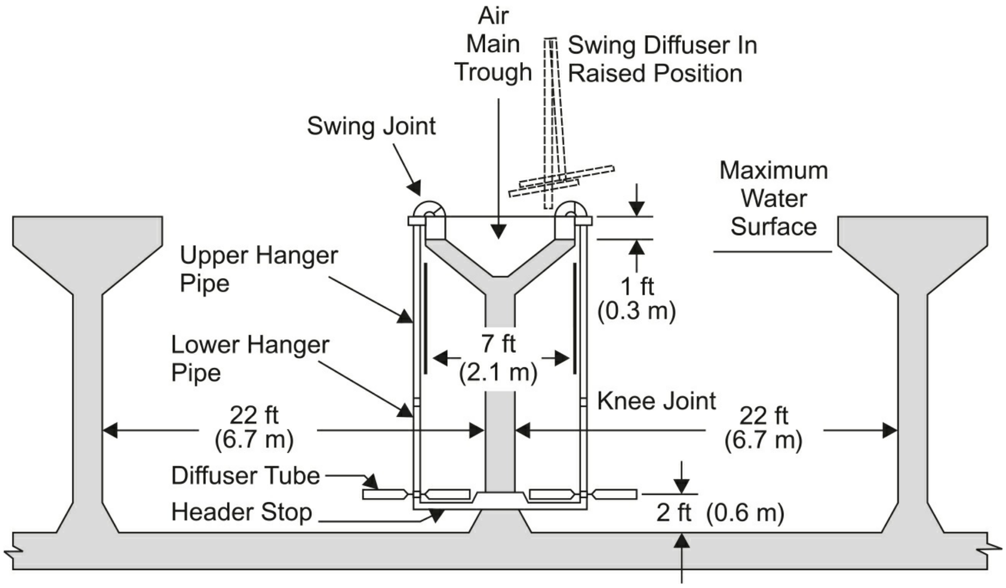

FIGURE 23.4 Cross section of typical activated sludge aeration tank.

The rectangular shape permits common-wall construction for multiple tanks. If total capacity exceeds 5000 ft^3 (142 m^3), the total aeration tank volume required should be divided among two or more units capable of independent operation. Total capacity required is determined from the biological process design.

If effluent is to be aerated with diffused air, geometry of the tank may significantly affect aeration efficiency and amount of mixing obtained. Depth of effluent in the tank should be between 10 and 16 ft (3–4.9 m), so that diffusers can work efficiently. Freeboard should be 1 to 2 ft (0.3–0.61 m) above the waterline. Width of the tank in relation to its depth is important, if spiral-flow mixing is used. The width-to-depth ratio for such tanks may vary from 1.0:1 to 2.2:1. This limits the width of a tank channel to 20 to 36 ft (6.1–11 m).

In large plants, channels become quite long, sometimes longer than 500 ft (152 m) per tank, and tanks may consist of one to four channels with round-the-end flow in multiple-channel tanks.

Large plants should contain not less than four tanks, and preferably six to eight or more. Some of the largest plants contain 30 to 40 tanks arranged in several groups or batteries.

Figure 23.4 is based on the use of coarse bubble air diffusers for transfer of oxygen to the liquid. Today, the use of fine bubble diffusers installed across the width and length of the aeration basin are preferred, to reduce energy use. In fact, many plants originally built with coarse bubble diffusers have been modified to fine bubble diffusers to reduce energy costs.

Secondary Clarifier

A secondary clarifier is constructed and operated very much like a primary clarifier, except that the secondary tank follows the biological treatment process (i.e., trickling filter or activated sludge). The function of secondary clarifiers varies with the method of biological treatment used. Clarifiers following trickling filters are used to separate biological solids that have broken away from the filter media. Clarifiers in an activated sludge system, however, serve two purposes. Besides providing a clarified effluent, they provide a concentrated source of return sludge to the aeration basin for process control.

Like primary clarifiers, secondary tanks may be round or rectangular. These tanks may be designed for natural settling or chemically aided settling, with tank size being related to one of the following:

- Surface loading rates in gallons per square foot (m^3/m^2) of floor area per day
- Solids loading rate in pounds (kilograms) of solids per square foot (m^2) of floor area per day
- Flow-through velocity in feet per minute (m/min) (rectangular tanks)
- Weir placement and loading rates in gallons (m^3) per day per linear foot (meter) weir length
- Retention time of settled sludge in hours

Clarifiers in activated sludge systems must be designed not only for hydraulic overflow rates, but also for solids loading rates (solids flux). This is because both clarification and thickening are needed in activated sludge clarifiers. At higher MLSS values (i.e., more than about 1500 mg/L), ability of the clarifier to thicken solids becomes the controlling factor. Solids loading rate becomes critical in determining tank size and operation limitations. As a result, design of clarifiers following the activated sludge process is usually based on average and peak overflow rates and solids loadings.

Performance of secondary effluent treatment systems is determined by comparing the quality of overflow from secondary clarifiers to that of incoming effluent. The biological treatment unit converts some of the soluble and insoluble organics to suspended organic solids. However, the treatment process is successful only if these organic solids are removed in the secondary clarifiers/thickeners. Secondary clarifier operational variables have the most critical effect on overall plant performance. Table 23.6 provides typical operational loading parameters of secondary clarifiers for treatment of various industrial effluents by biological treatment.

	Solids Flux		Overflow Rate	
Industry	**lb/(d·ft^2)**	**kg/(d·m^2)**	**gpd/ft^2**	**m^3/(d·m^2)**
Pulp and paper	18–25	88–122	400–800	16–33
Petrochemical	10–15	49–73	300–600	12–24
Refinery biological contactor	8–12	39–59	300–600	12–24
Secondary	20–29	98–142	400–800	16–33
Nitrified effluent	17–24	83–117	400–600	16–24

TABLE 23.6 Typical Biological Secondary Settling Tank Operational Loading Parameters

Aeration Equipment

The three basic methods of aerating effluent are:

1. Introduce air or oxygen into effluent with submerged porous diffusers.
2. Agitate effluent mechanically to promote solution of oxygen from the atmosphere above the liquid being aerated (mechanical aerator).
3. Use aspirators (eductors) with or without blowers (jet aeration).

The amount of air used per pound (kilogram) of BOD removed varies greatly from one plant to another and for different industries. Comparing air use at different plants is risky because of different loading rates, control criteria, biological treatment rates, and operating procedures.

Diffused Aeration A diffused air system consists of diffusers that are submerged in effluent, header pipes, air mains, and blowers and appurtenances through which air is supplied.

The diffusers most commonly used in aeration systems are designed to produce fine, medium, or coarse (relatively large) bubbles (see Table 23.7). Fine bubble diffusers constructed of neoprene and other materials are most commonly used today due to their high oxygen transfer efficiency (lower power consumption).

Bubble Size	Transfer Efficiency	Description
Fine	High	Ceramically bonded grains of fused crystalline aluminum oxide. Vitreous silicate bonded grains of pure silica. Resin bonded grains of pure silica.
Medium	Medium	Plastic wrapped diffuser tubes Woven fabric sock or sleeve diffusers
Coarse	Low	Various orifice devices Sparger air escapes from periphery of flexible or rigid disc that is displaced when manifold pressure exceeds the head on the disc. Slot orifice injectors

TABLE 23.7 Description of Diffuse Air Aeration Devices

Mechanical Aerators The most commonly used types of mechanical aerators are surface and submerged turbine aerators. With surface aerators, oxygen is entrained both from the atmosphere and from air or pure oxygen introduced in the tank bottom. In either case, the pumping action of the aerator, and that of the turbine, help to keep the contents of the aeration tank mixed. Both types are described here, along with aerator performance and energy required for mixing.

Surface Aerators—Mechanical surface aerators are the simplest type of aerators (see Figs. 23.5–23.7). They are available in sizes from 1 to 100 hp (0.75–75 kW). They consist of submerged or partially submerged impellers that are attached to motors, which are mounted on floats or fixed structures. Impellers are fabricated from steel, cast iron, noncorrosive alloys, and fiberglass-reinforced plastic, which are used to agitate effluent vigorously, entraining air in the effluent and causing a rapid change in the air-water interface to facilitate solution of oxygen. Surface aerators may be classified as low or high spec, according to the speed of rotation of the impeller. In low-speed aerators, the impeller is driven through a reduction gear by an electric motor. Motor and gearbox are usually mounted on a platform that is supported either by piers extending to the bottom of the tank, or by beams that span the tank. They have also been mounted on floats. The propeller for high-speed aerators is driven at the electrical motor speed. The high speed of the propeller and the smaller diameter (as compared to low-speed units) results in lower oxygen transfer efficiency.

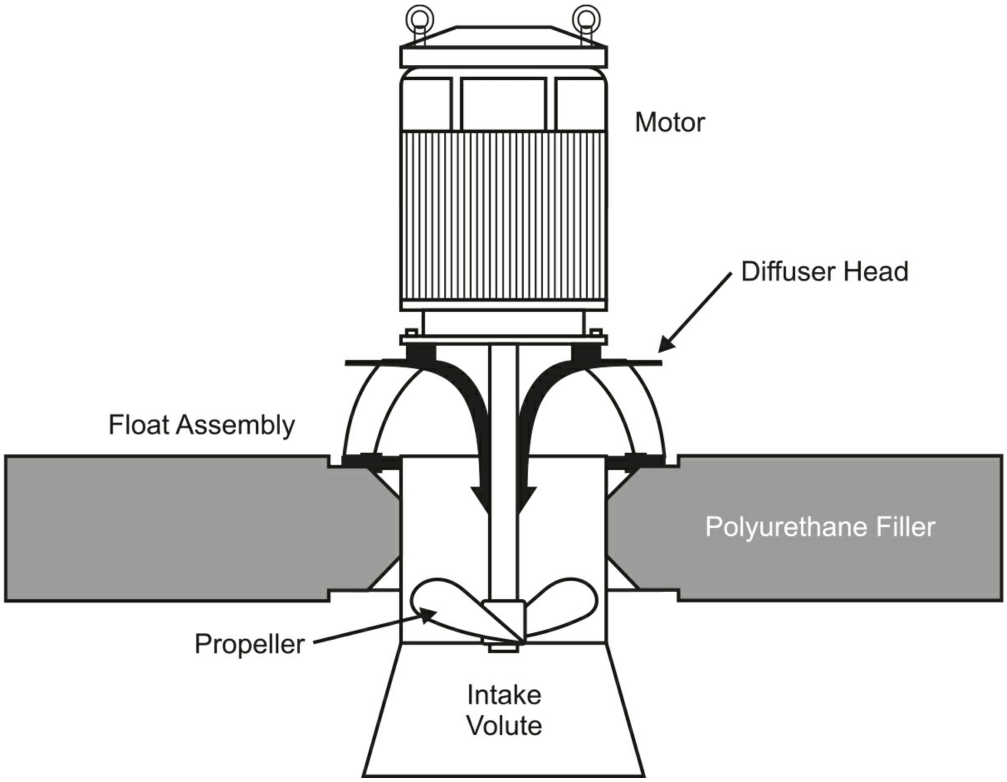

FIGURE 23.5 Surface mechanical aerator.

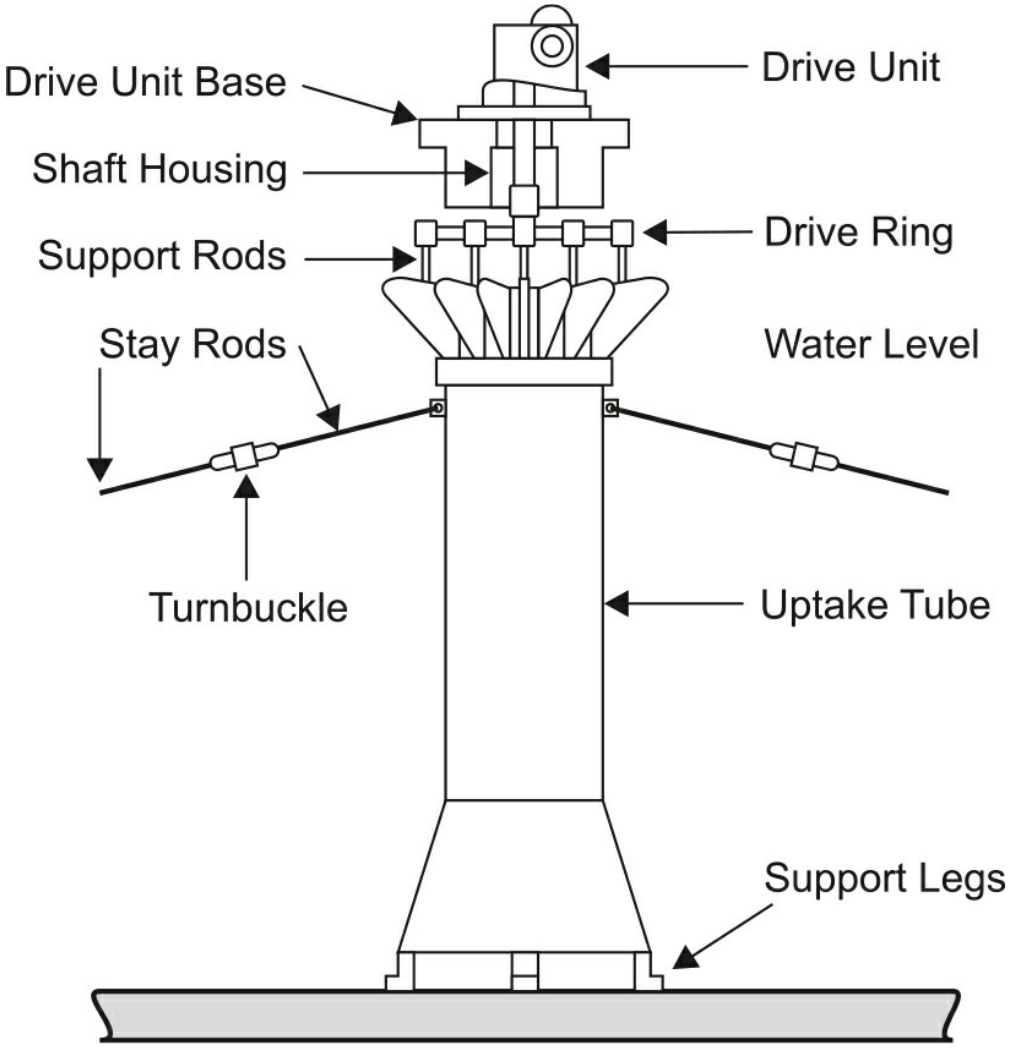

FIGURE 23.6 Simplex cone mechanical aerator.

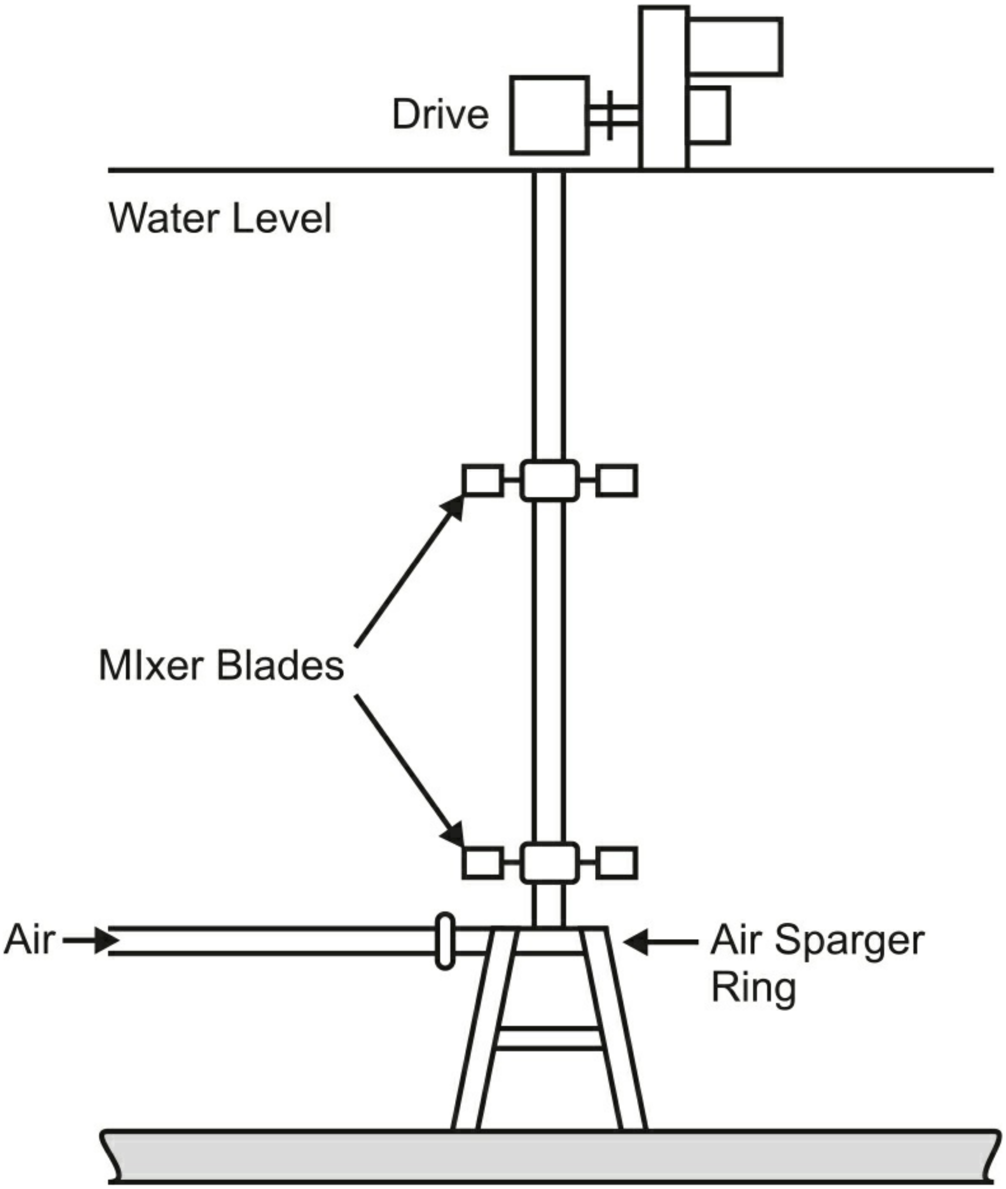

FIGURE 23.7 Turbine mechanical aerator.

Submerged Turbine Aerators—Most mechanical surface aerators are upflow types that rely on violent agitation of the surface, and air entrainment for oxygen transfer efficiency. However, with turbine aerators, air or pure oxygen may also be introduced by diffusion into the effluent beneath the impeller of downflow or radial aerators. (Not commonly used due to low transfer efficiency.) The impeller is used to disperse air bubbles and mix the tank contents. A draft tube may be used with either upflow or low-speed models in deep aeration tanks. The draft tube is a cylinder with flared ends mounted concentrically, with the impeller extending from just above the floor of the aeration tank to just beneath the impeller.

Mechanical Aerator Performance—Surface aerators are rated in terms of their oxygen transfer rate expressed as pounds (kilograms) of oxygen per horsepower-hour (kilowatt-hour) at standard conditions, which exist when the temperature is 68°F (20°C), initial DO is 0.0 mg/L, and test liquid is tap water. Commercial-size surface aerators now available range in efficiency from 2 to 3.5 lb O_2/[hp · h] (1.2–2.1 kg/kWh) at standard conditions. The lower value is for motor speed aerators, while the higher is for low-speed units.

Energy Requirement for Mixing—As with diffused air systems, size and shape of the aeration tank are very important, if good mixing is to be achieved. Aeration tanks may be square or rectangular and may contain one or more units. Water depth may vary from 4 to 12 ft (1.2–3.7 m) when using surface aerators. Depths up to 35 ft (10.7 m) have been used with draft-tube mixers.

In diffused air systems, the air requirement to ensure good mixing varies from 20 to 30 ft^3/1000 ft^3 (20–30 m^3/1000 m^3) of tank volume.

Typical power requirements for maintaining a completely mixed flow regime with mechanical aerators vary from 0.6 to 1.15 hp/1000 ft^3 (16–30 kW/1000 m^3), depending on design of the aerator and geometry of the tank, lagoon, or basin. In the design of aerated lagoons for treatment of domestic wastes, it is extremely important that the mixing power requirement be checked, because in most instances it is the controlling factor. With both the diffused air systems and mechanical aerators, power required for oxygen transfer is usually less than that required for mixing to keep solids in suspension.

Jet Aeration Jet aeration consists of an eductor (aspirator) pump and blower. Pump suction is from the aeration basin and discharges to the inlet of the eductor. The blower supplies air to the venturi throat of the eductor. Water velocity through and size of the venturi throat creates small air bubbles for efficient oxygen transfer to liquid in the aeration basin. It has been found in some cases that pumping biological flocs through the eductor breaks up the floc, resulting in solids carryover from secondary clarifiers.

Table 23.8 shows typical performance characteristics for air diffusers used in effluent treatment.

Type of Aerator	Water Depth, ft (m)	Oxygen Transfer Efficiency, %	Aerator Rating	
			lb O_2/(hp·h)	kg O_2/kWh
Fine bubble:				
Tubes-spiral roll	15 (4.6)	15–20	6–8	3.6–4.9
Domes-full floor coverage	15 (4.6)	25–35	11–12.5	6.7–7.6
Coarse bubble:				
Tubes	15 (4.6)	10–13	4–5	2.4–3
Spargers	14.5 (4.4)	6–8	2–3.5	1.2–2.1
Jet aerators	15 (4.6)	15–24	4–5	2.4–3
Static aerators	15 (4.6)	10–11	4–4.5	2.4–2.7
Surface aerators:				
Low speed	12 (3.7)	–	3–3.5	1.8–2.1
High speed	8 (2.4)	–	2–2.5	1.2–1.5

TABLE 23.8 Air Diffuser Performance Characteristics

Oxygen Equipment

There are two pure oxygen generator designs: the traditional cryogenic air separation process for large applications and a pressure swing adsorption (PSA) system for the somewhat smaller and more common plant sizes.

The cryogenic air separation process involves liquefaction of air, followed by fractional distillation to separate it into its components (mainly nitrogen and oxygen).

The PSA system uses a multibed adsorption process to provide a continuous flow of oxygen gas. Feed air is compressed and passed through one of the adsorbers. The adsorbent removes carbon dioxide, water, and nitrogen gas, and produces relatively high-purity oxygen. While one bed is adsorbing, the others are in various stages of regeneration.

The concept of the PSA generator is that oxygen is separated from feed air by adsorption at high pressure, and the adsorbent is regenerated by “blowdown” to low pressure. The process operates on a repeated cycle having two basic steps: adsorption and regeneration.

Activated Sludge Process Control Concepts

Common control methods used for the activated sludge process include:

- Solids retention time (SRT)
- Food-to-microorganism ratio (F/M)
- Constant MLSS
- Return activated sludge control

Objectives of activated sludge secondary treatment are to biologically oxidize waste organic content aerobically and to remove excess new cell growth solids before discharge to receiving waters. Each treatment plant operates within a range of process control parameters based on original plant design that tends to keep the biological process in a steady state condition, as long as raw waste influent characteristics do not change too abruptly. By maintaining process parameters within a narrow range, swings in process efficiency that may result from shock loads or upsets are minimized, and continuously high organic removal efficiency is assured.

Solids Retention Time

Solids retention time (SRT), also called MCRT or sludge age, is calculated by dividing the total quantity of sludge in the aeration basin and clarifier by daily sludge losses through waste activated sludge and effluent. Equation (23.9) shows the calculation:

$$\mathrm{SRT} = \frac{X_1 V_1 + X_2 V_2}{X_X Q_X + X_e Q_e} \tag{23.9}$$

where SRT = solids retention time, days
X_1 = MLSS in aeration basin, mg/L
X_2 = MLSS in clarifier, mg/L
X_x = MLSS in waste activated sludge, mg/L
X_e = MLSS in effluent, mg/L
V_1 = volume of aeration basin, gal (m^3)
V_2 = volume of clarifier, gal (m^3)
Q_x = effluent flow rate, gpd (m^3/d)
Q_e = waste activated sludge flow rate, gpd (m^3/d)

The activated sludge system can be controlled based on keeping the SRT value at a constant level. (See Table 23.9 for recommended ranges for activated sludge processes.)

Process Description	Flow Regime	SRT, days	F/M[*]	Aerator Loading[†]	MLSS, mg/L	Detention Time, h	Recirculation Ratio
Conventional	Plug flow	5–15	0.2–0.4 (0.1–0.2)	20–40 (320–640)	1500–3000	4–8	0.25–0.5
Complete mix	Complete mix	5–15	0.2–0.6 (0.1–0.3)	50–120 (800–1920)	3000–6000	3–5	0.25–1.0
Step aeration	Plug flow	5–15	0.2–0.4 (0.1–0.2)	40–60 (640–960)	2000–3500	3–5	0.25–0.75
Contact stabilization	Plug flow	5–15	0.2–0.6 (0.1–0.3)	30–75 (480–1200)	1000–4000[§] 4000–10 000	0.5–1.5[§]	0.5–1.5
Extended aeration	Complete mix	20–30	0.05–0.15 (0.02–0.07)	10–15 (160–240)	2000–6000	24	0.5–2.0
Pure oxygen systems	Complete mix, reactors in series	8–20	0.25–1.0 (0.1–0.5)	100–250 (1600–4000)	4000–8000	2–5	0.25–0.5
Aerated lagoon	Complete mix	5–120	[‡]	[‡]	2000–6000	120–1000	0

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[*] lb BOD$_5$ MLVSS/d (kg/d).

[†] lb BOD$_5$/1000 ft^3 (kg/1000 m^3) tank volume.

[‡] Depends on waste loading.

[§] Contact unit.

[¶] Stabilization tank.

TABLE 23.9 Summary of Operating Data for Activated Sludge Processes

If SRT overly exceeds the recommended range, which directly means scarce food condition or low F/M ratio, sludge floc can be dismantled, and pin floc can be formed. This condition is often accompanied by solids loss and an increase in effluent turbidity from the secondary clarifier.

When the system is operated at lower than recommended SRT, a condition commonly called “young sludge” may result. This light, fluffy, buoyant sludge, also called straggler floc, settles slowly. This is witnessed in a clarifier when these fluffy floc particles are pulled over weirs even though the effluent may be relatively clear. This condition may appear in the aeration basin as white billowy foam. These conditions are typical of activated sludge systems just after startup. In addition, SRT lower than five days is not sufficient to grow enough slowly growing autotrophic microorganisms that oxidize nitrogen. Consequently, nitrification is not possible at low SRT.

The main variable in SRT control is sludge wasting rate. Generally, operation involves finding an SRT level at which the plant achieves optimum effluent quality. When the SRT value has been reduced to proper levels and conditions in the treatment system improved, then operator stops or decreases the sludge-wasting rate to maintain constant SRT. There are conditions and periods depending on loading rates, changes in flow rates, and presence of toxic shocks, where SRT levels should be increased or decreased.

Food-to-Microorganism Ratio

A term for expressing organic loading of an activated sludge process is F/M ratio, and is a critical factor in process design and operation, especially in determining aeration basin volume. F/M is usually defined as:

$$\mathrm{F/M} = \frac{Q_0(S_0 - S_e)}{X_A V_A} \tag{23.10}$$

where F/M = food-to-microorganism ratio, lb BOD/(lb MLVSS · d) [kg BOD/(kg MLVSS · d)]
Q_0 = influent flow rate, gpd (m^3/d)
S_0 = influent BOD_5, mg/L
S_e = effluent BOD_5, mg/L
X_A = mixed liquor volatile suspended solids (MLVSS) in aeration basin, mg/L
V_A = aeration basin volume, gal (m^3)

If only COD is available for domestic effluent, divide the COD by 1.5 to obtain approximate BOD_5. Similarly, MLSS can be multiplied by 0.75 to obtain an approximate MLVSS. BOD/COD and MLSS/MLVSS ratios for industrial effluent can vary significantly depending on the type of industrial process.

F/M and MLVSS are important design criteria for sizing the aeration basin and along with sludge age are important operating criteria.

Mixed Liquor Suspended Solids and Mixed Liquor Volatile Suspended Solids

Suspended solids level is one of the most important control parameters in biological effluent treatment processes. It is not only directly related with sludge settling properties and effluent quality, but also related with F/M ratio that is in turn related with all aspects of sludge properties.

In general, MLSS represent TSS, irrespective of biological activity. Measurement is expressed as an empirical test result that reports the quantity of suspended solids carried in the aeration basin. Usually, glass filters having a pore size of 1.2 μm are used.

On the other hand, MLVSS represent the organic portion of MLSS, which is used to represent biomass. This is also expressed as an empirical test result (the amount of solids that was lost in volatilization at 550°C); this test reports roughly the portion of MLSS that has the active microbial population used to absorb and degrade soluble organic matter in wastes.

The activated sludge system can be controlled based on a constant MLSS level much the same way as the SRT control approach. (See Table 23.9 for recommended ranges for activated sludge processes.) Similar conditions occur in the process due to MLSS concentrations higher and lower carried in the activated sludge system (as described for respective conditions for SRT levels). As with SRT control, the main variable for maintaining constant MLSS is the sludge-wasting rate. After an acceptable MLSS level is determined for operation of the system, the sludge-wasting rate is controlled to maintain this level. When the MLSS level increases above the determined optimum range, then the plant operator starts or increases the sludge-wasting rate. When the MLSS level decreases below the range, then the operator stops or decreases the sludge-wasting rate, to maintain a constant MLSS level in the system and F/M in the optimum range.

Sludge Blanket Depth

Sludge blanket depth in the clarifier should be measured at the same time each day and at the same point on the clarifier bridge. The best time is during the period of maximum daily flow, because the clarifier is operating under the highest solids loading rate. Adjustments in the recycle activated sludge (RAS) flow rate should be needed only occasionally if the activated sludge process is operating properly.

An additional advantage of monitoring sludge blanket depth is that problems, such as improperly operating sludge collection equipment, can be observed due to irregularities in blanket depth. A plugged pick-up on a clarifier sludge collection system would cause sludge depth to increase in the area of the pick-up, and decrease in areas where properly operating pick-ups are located. These irregularities in sludge blanket depth are easily monitored by measuring profiles of blanket depth across the clarifier.

Other Parameters Used to Evaluate Performance

Other parameters can be used to track performance of the activated sludge process. These parameters are also effective in assessing health of microorganisms and can be used to determine where problems exist. Some common parameters are:

- Sludge volume index (SVI)
- Oxygen uptake rate
- Microscopic examination
- Aerator loading
- Detention time
- Mixed liquor DO level

Sludge Volume Index This index is defined as the volume (in milliliters) occupied by one gram of activated sludge mixed liquor solids, dry weight, after settling for 30 minutes in a 1000 mL graduated cylinder. In practice, it is taken to be the percent volume occupied by the sludge in a mixed liquor sample (taken at the outlet of the aeration tank) after 30 minutes of settling, divided by the suspended solids concentration of the mixed liquor. The formula is expressed as:

$$\mathrm{SVI} = V_s/\mathrm{MLSS} \qquad (23.11)$$

where SVI = sludge volume index, mL/g MLSS
V_s = volume of settled sludge after 30 minutes, mL/L
MLSS = mixed liquor suspended solids, g/L

SVI has been used as an indication of the settling characteristics of the sludge. However, SVI that is characteristic of good settling sludge varies with the type of industrial waste and concentration of mixed liquor solids, and observed values at a given plant should not be compared with those reported for other plants or in the literature. Typical SVI for good settling sludge with mixed liquor concentrations is in the range of 1500–3500 mg/L are:

- SVI of 80–120 is normal and considered good settling.
- SVI greater than 120 is an indication of possible bulking in the clarifier.
- SVI less than 80 is an indication very compact and heavy floc.

Dissolved Oxygen Uptake DO uptake is determined from a short duration DO test measurement in a standard 300 mL BOD_5 bottle, using oxygen saturated samples of fresh aerator mixed liquor, return sludge, bioreactor influent, or a mixture of bioreactor influent, plus a portion of return sludge. Results are typically taken once or twice a shift by treatment plant operators, and the results are usually graphed.

$$\text{OUR} = (\text{DO}_0 - \text{DO}_{10})(60\ \text{min}/h)/10 \tag{23.12}$$

$$\text{MLRR} = \text{OUR}/\text{MLVSS} \tag{23.13}$$

where OUR = oxygen uptake rate, mg $O_2/(L \cdot h)$
DO_0 = initial DO at time zero, mg/L
DO_{10} = DO after 10 minutes, mg/L
MLRR = mixed liquor respiration rate, mg $O_2/(g\ MLVSS \cdot h)$
MLVSS = mixed liquor volatile suspended solids, g/L

Results are typically used to evaluate factors such as aeration system capacity limitations, mixed liquor solids levels, bioreactor raw water treatability, immediate DO demand, reactivity of raw wastes, and return sludge thickening time limits for maintaining viable mixed liquor microorganisms in the secondary clarifier.

The respiration rate tells an operator about the state of health of activated sludge mixed liquor. The respiration rate of a normal steady-state operational activated sludge plant changes from season to season.

Interpretation of these results is straightforward. A typical respiration rate in a sludge sample from the beginning of the aeration tank is between 12 and 20 mg $O_2/(g\ MLVSS \cdot h)$. Higher rates indicate high organic loading, while lower rates indicate low loading. Respiration rates higher than normally observed suggest increases in reactor BOD loadings or F/M. High respiration rates [usually more than 35–45 mg $O_2/(g\ MLVSS \cdot h)$] are usually characteristic of young mixed liquor that is under oxidized. Comparison of oxygen uptake rate of mixed liquor with that of secondary effluent usually shows high effluent uptake rate [20–30 mg $O_2/(L \cdot h)$ for secondary effluent is high]. High results should be compared with settling or compaction rates of mixed liquor solids and foaming tendencies, since these results tend to be related when mixed liquor solids are young and under aerated.

Lower than normal respiration rates indicate one of three things:

1. SRT is longer than usual.
2. BOD loading has dropped off, decreasing F/M.
3. Some type of biological inhibitory agent is present in the waste.

Low respiration rate should be checked right away with oxygen uptake results for all four samples. Healthy activated sludge has an oxygen uptake rate of 8 to 20 mg $O_2/(L \cdot h)$ for a sample of mixed liquor. When levels drop below this range, it can be an indication of biological toxicity in the reactor, dictating the need for specific action.

Mixed Liquor Dissolved Oxygen Mixed liquor DO level in activated sludge aeration basins is controlled by:

- Organic loading directly influences oxygen uptake rate, which indirectly affects DO level.
- Aeration source and level directly influence DO level.
- Mixed liquor solids inventory indirectly influences oxygen uptake rate and F/M ratio, which in turn indirectly affect mixed liquor DO level.

DO levels in the effluent from the aeration tank are generally maintained between 1.0 and 2.0 mg/L or higher, depending on the process.

Nutrient Removal in Activated Sludge

In water environments such as rivers, lakes, and oceans, the most stringent nutrient for algal growth is phosphorous. Therefore, controlling phosphorous in the water environment is the single most effective means to maintain clean water and prevent eutrophication (algae growth). In addition to phosphorous, nitrogen is the next most stringent nutrient, though some algae can fix gaseous nitrogen in air. While there are many forms of nitrogen in terms of oxidation state, ammonia nitrogen is the most readily utilized form for most organisms that contaminate water. In addition, ammonia nitrogen consumes DO and may suffocate fish and higher life forms, when it is biologically oxidized. Both are important, although controlling ammonia nitrogen is given higher priority than controlling nitrate nitrogen.

In biological effluent treatment, some part of phosphorous and nitrogen can be converted to biomass and eventually removed through sludge wastage. Microorganisms treating effluent contain 1.7% phosphorous and 8.7% nitrogen. If SRT and other conditions are properly managed, the majority of ammonia and organic nitrogen can be oxidized to nitrate, which is less harmful to the water environment. Phosphorous and nitrogen removal can be further enhanced biologically using cyclic DO conditions.

Phosphorous Removal

If sludge containing many kinds of different microorganisms is circulated periodically between low anaerobic and high DO conditions, some species that can adapt well in this cyclic DO condition will have advantage over other microorganisms. While most heterotrophic microorganisms can make energy under the oxygen rich environment, some microorganisms [polyphosphate accumulating organisms (PAO)] can make energy without oxygen by hydrolyzing the polyphosphate accumulated in the cell.

If PAO are circulated between DO rich and anaerobic conditions periodically, they accumulate excess phosphorous during DO rich conditions to prepare for the DO scarce conditions. During DO scarce conditions, PAO absorb fatty acids in the liquid phase and store them in the form of polyhydroxybutyrate (PHB), which is used to produce new PAO during DO rich conditions.

Phosphorous accumulation during DO rich conditions is often called "luxury uptake." Under aerobic conditions, more phosphorous is accumulated by PAO to prepare for anaerobic conditions. Moreover, during anaerobic conditions, PAO have a clear advantage in survival over other microorganisms.

Phosphorous can be also removed chemically. Addition of chemicals to the secondary clarifier for phosphate precipitation is commonly practiced. A mineral salt addition involving Fe^{+3} or Al^{+3} combines with soluble orthophosphate available and precipitates as insoluble metal phosphates. Chapter 24 describes dosages for phosphorus removal by chemical addition. However, adding acid salts of these metals neutralizes alkalinity of waste and drops pH.

Reduction in alkalinity sometimes inhibits biological treatment in the activated sludge process. In addition, formation of a substantial amount of insoluble iron or aluminum hydroxide can increase sludge handling and dewatering costs significantly.

In these cases, where chemical phosphorus removal is intended to take place in activated sludge, tests should be run to see if sodium aluminate can be substituted for acid metal salts of iron or aluminum. Reactions and products of typical phosphorus removal agents for this type of application are summarized in Chap. 24. Solubility of metal salts used in phosphorus precipitation is strongly pH dependent. Figure 24.1 in Chap. 24 shows solubility of iron and aluminum phosphate versus pH.

Nitrogen Removal

Nitrogen removal can be achieved as follows:

$$NH_4^+ \xrightarrow{O_2} NO_2^- \xrightarrow{O_2} NO_3^- \xrightarrow{BOD} N_2(gas)\uparrow \tag{23.14}$$

Nitrification occurs by autotrophs in aerobic conditions with consumption of DO. All biological processes having oxygen rich stages and long sludge age can oxidize ammonia nitrogen to nitrate as follows:

$$2NH_4^+ + 3O_2 \xrightarrow{\text{Nitrosomonas}} 2NO_2^- + 2H_2O + 4H^+ \tag{23.15}$$

$$2NO_2^- + O_2 \xrightarrow{\text{Nitrobacter}} 2NO_3^- \tag{23.16}$$

Denitrification occurs in the absence of free oxygen (anoxic condition). Most heterotrophs can respire with consumption of combined oxygen in the form of nitrate, nitrite, hypochlorite, etc.

$$2NO_3^- + 2H^+ \longrightarrow N_2(gas)\uparrow + H_2O + 2.5O_2 \tag{23.17}$$

In the first nitrification process [Eqs. (23.15) and (23.16)], autotrophic microorganisms (nitrifiers) oxidize ammonia nitrogen to nitrate with consumption of DO. Then [Eq. (23.17)] nitrate is reduced to nitrogen gas in anoxic tanks, where heterotrophic microorganisms deliver oxygen from combined oxygen sources such as nitrate due to a lack of elemental oxygen.

In terms of kinetics, nitrification is much slower than denitrification.

Autotrophs not only grow slower than heterotrophs, but the amount of food for autotrophs (nitrogen) is scarcer than that for heterotrophs (BOD). Autotroph concentration is normally less than 10% of the total bacterial population. Consequently, if SRT is lower than five days, autotrophs rarely build up to a sufficient level due to washout. Moreover, autotrophs are more sensitive to temperature. Nitrification can be severely affected below 50°F (10°C), except in cases where MLSS is very high such as in membrane bioreactor (MBR) processes in which MLSS is around 10 g/L.

Since combined oxygen in nitrate is utilized during BOD oxidation by heterotrophs, a certain amount of BOD is necessary to reduce nitrate. Theoretically, the BOD/TKN ratio should be at least 3.4:1 to denitrify all nitrogen. If the ratio is lower than 3.4:1, nitrogen removal is limited to some extent depending on BOD deficiency. In these cases, a source of carbon such as methanol is added to the denitrification basin.

In the activated sludge process, pH in the aeration basin often decreases below the optimum range (6.5–7.5) mainly due to formation of nitrates during oxidation of TKN (ammonia nitrogen plus organic nitrogen) contained in the influent. In theory, 1 mg nitrogen can consume 3.6 mg alkalinity as $CaCO_3$, if it is not denitrified. However, when denitrification is performed, net acid formation by nitrification can be reduced, and pH can be maintained more easily.

Aerated Lagoons

Aerated lagoons or ponds evolved from facultative stabilization ponds when surface aerators were installed to overcome odors from organically overloaded ponds.

In an aerated lagoon, all solids are maintained in suspension. Aerated lagoons are operated as flow-through activated sludge systems without recycle, usually followed by large settling ponds. Lagoons and stabilization ponds are currently in use in older plants but are out of favor for new construction due to:

- Odors from algae blooms
- Groundwater contamination concerns because they are only clay lined
- Large land area requirements

Seasonal continuous nitrification may be achieved in aerated lagoon systems. The degree of nitrification depends on design and operating conditions within the system and on effluent temperature. Generally, with higher effluent temperatures and lower loadings (increased SRT), higher degrees of nitrification can be achieved.

Significant Operational Control Parameters

Aerated lagoons followed by a clarifier with sludge recycle are very similar to activated sludge systems with respect to operation and control.

An aerated lagoon is usually deeper than a facultative pond. Mechanical or diffused aerators provide most of the DO required and mix lagoon contents. Turbulence levels should be high enough to ensure uniform DO and suspended solids concentrations throughout. The higher the rate of oxygen transfer to the system, the more intense the mixing in the pond, and subsequently, the less pronounced the tendency for sedimentation. Factors that must be considered in the operation of aerated lagoons are similar to those of the activated sludge process and include: biological solids produced SRT, BOD removal, pond mixing, and temperature effects.

Biological Solids

High-rate aerated lagoons can generate 0.6 to 0.7 lb (0.27–0.32 kg) of suspended solids per pound (kilogram) of BOD_5 removed.

Solids Retention Time

The basis of operation for an aerated lagoon is SRT. Typical SRT design values for aerated lagoons used for treating low-strength industrial wastes vary from 3 to 6 days. Aerated lagoons used in paper mills, refineries, and petrochemical plants have SRT of 10 to 20 days; these generally operate in the extended aeration mode.

Biochemical Oxygen Demand Removal

Aerated lagoons that are properly designed operated and maintained, can produce effluent that is low in solids and with effluent BOD_5 of less than 30 mg/L. Solids concentrations in effluent are variable (20–100 mg/L) and are affected by seasonal changes.

pH and Alkalinity Balance

In general, aerated lagoons operate most satisfactorily in the pH range of 7.2 to 7.8. To achieve desired pH, influent waste pH should be maintained from 6.5 to 8.3.

Oxygen Requirement

Based on operating results obtained from a number of industrial and domestic installations, the amount of oxygen required varies from 0.7 to 1.4 times the amount of BOD_5 removed.

Temperature

The two most important effects of temperature are, reduced biological activity and treatment efficiency, and formation of ice.

Icing effects may be minimized by increasing the depth of the lagoon or by altering the method of operation. Reducing the area by one-half increases effluent temperature. This action corresponds roughly to about a 50% increase in the rate of biological activity.

Stabilization Ponds

A stabilization pond (also called an oxidation pond) is a relatively shallow body of water contained in an earthen basin of controlled shape, designed for treating effluent. Ponds in the past were used extensively for treatment of industrial effluent and mixtures of industrial and domestic effluent that are amenable to biological treatment. Installations are now serving such industries as oil refineries, slaughterhouses, dairies, poultry processing plants, and rendering plants. New regulations, which require double lining of effluent lagoons that contain specific toxics such as benzene, will limit continued usage of these systems in the future.

Pond Classification

Stabilization ponds are usually classified according to the nature of biological activity taking place: aerobic, anaerobic, or combined aerobic–anaerobic (facultative). Principal types of stabilization ponds in common use are shown in Table 23.10. Other classification schemes used are based on the type of influent (untreated, screened, settled effluent, or activated sludge effluent);

pond overflow condition (nonexistent, intermittent, or continuous); and method of oxygenation (photosynthesis, atmospheric surface reaeration, or mechanical aerators).

Type of Pond or Pond System	Common Name	Identifying Characteristic	Application
Aerobic (0.5–2 ft) (0.2–0.6 m)	High-rate aerobic pond		Nutrient removal, treatment of soluble organic wastes, conversion of wastes.
Aerobic (2–5 ft) (0.6–1.5 m)	Low-rate aerobic pond	Designed to maintain aerobic conditions throughout the liquid depth.	Treatment of soluble organic wastes and secondary effluents.
	Maturation or tertiary pond	Similar to low-rate aerobic ponds but very lightly loaded.	Used for polishing (upgrading) effluents from conventional secondary treatment processes, such as trickling filter or activated sludge.
Aerobic–anaerobic	Facultative pond	Deeper than a high-rate pond. Photosynthesis and surface reaeration provide oxygen for aerobic stabilization in upper layers. Lower layers are facultative. Bottom layer of solids undergoes anaerobic digestion.	Treatment of screened or primary settled effluent and industrial wastes. Secondary effluent polishing
Aerobic–anaerobic	Facultative pond with mechanical surface aeration	As above, but small mechanical aerators are used to provide oxygen for aerobic stabilization.	Treatment of screened or primary settled effluent and industrial wastes. Secondary effluent polishing

TABLE 23.10 Types and Applications of Stabilization Ponds