

CHAPTER 49

WATER TREATMENT: DEPOSITION, CORROSION, AND BIOLOGICAL CONTROL

<i>Water Characteristics</i>	49.1	<i>Biological Growth Control</i>	49.11
<i>Alternative Water Sources</i>	49.2	<i>Cooling Tower Systems Start-Up and Shutdown</i>	49.14
<i>Deposition, Scale, and Suspended-Solids</i>		<i>Heating and Steam-Generating Systems</i>	49.15
<i>Control</i>	49.3	<i>Selection of Water Treatment</i>	49.18
<i>Corrosion and Corrosion Control</i>	49.6	<i>Terminology</i>	49.21

THIS chapter covers the fundamentals of water treatment. It provides guidance on the treatment of water and water-based fluids used in heating, air-conditioning, refrigeration, and process systems, with a focus on the control of corrosion, scale, fouling, and biological growth. Proper treatment improves the performance and energy efficiency of these systems while helping to protect human health and safety. Water treatment also extends the life of equipment in both open- and closed-loop systems. In addition, water treatment can help conserve water resources as well as enable the use of alternative sources of water. All of these benefits help to promote a healthier, more sustainable environment.

1. WATER CHARACTERISTICS

Although water is a common material, it has unique properties that make it ideal for heating, cooling, and steam generating processes. Water is the only common substance that exists in all three states of matter [solid (ice), liquid (water), and gas (steam)] at normal earth temperatures. Water absorbs more heat for a given temperature rise than any other common inorganic substance. Water expands 1600 times as it evaporates to form steam at atmospheric pressure. The steam is capable of carrying large quantities of heat. These unique properties of water make it an ideal material for heating, cooling, and power-generating processes.

All water contains varying amounts of impurities that can cause scale, corrosion, and other problems in industrial equipment. It takes on some of the characteristics of its surroundings as it dissolves minerals and picks up impurities from the air, soil, and vegetation or other materials it contacts. For that reason, water is often referred to as the **universal solvent**. When rain falls, it dissolves carbon dioxide and oxygen in the atmosphere. The carbon dioxide mixes with the water to form carbonic acid (H_2CO_3). When carbonic acid contacts soil that contains limestone ($CaCO_3$), it dissolves the calcium to form calcium bicarbonate. Calcium carbonate in water used in heating or air-conditioning applications can eventually become scale, which can increase energy costs, maintenance time, and equipment shutdowns, and can eventually lead to equipment replacement.

Water's composition changes as it is transported in pipelines, heated to make steam, or evaporated for cooling or other heat exchange processes. Impurities in water may reach a solubility limit and be deposited along the way, or water may corrode the metal equipment containing it. The actions of water in HVAC systems depend on the impurities in it and the temperatures and pressures to which it is subjected, as well as aspects of the systems where it is used. This provides a basis for many stability index calculations that are done on water to predict its corrosive and/or scaling tendency in water systems. The Langelier Saturation Index and Ryznar Stability Index, referred to as LSI and RSI respectively, are examples of

calculated indices often used in water treatment. For a proper evaluation, it is necessary to determine the impurities water contains, what problems these impurities may cause, and how they can be mechanically or chemically reduced, removed, or treated.

The following paragraphs present the more important chemical and physical properties or characteristics of water relevant to water treatment and that affect its use in HVAC applications.

Hardness refers to the amount of calcium and magnesium (typically expressed in ppm, as $CaCO_3$) in the water. It is a historical term referring to hard calcium and magnesium carbonate scales, such as those found in improperly treated boilers and cooling-water systems. Hardness contributes to scale formation, because its presence encourages deposition of calcium carbonate, or lime scale. Because the solubility of most calcium and magnesium salts decreases with an increase in temperature, these salts tend to form scale on heat transfer surfaces where the metal skin temperature is greater than the bulk water temperature. The amount of calcium and magnesium equivalent to the alkalinity in a solution is called **temporary hardness**. The excess calcium and magnesium, if any, is called **permanent hardness**. Boiler and cooling-water treatment programs must control the deposition of hardness salts using pretreatment removal (such as with boiler makeup or feedwater softening) or internal conditioning to solubilize and remove or otherwise control deposition.

Alkalinity is a measure of the capacity of water to neutralize strong acids. It is the measured carbonate and bicarbonate minerals (calculated as calcium carbonate, $CaCO_3$), and refers to the primary alkaline earth mineral contributing to alkalinity. Alkalinity is also measured and calculated as the hydroxide ion (OH^-), when present. All natural waters contain some quantity of alkalinity. The presence of alkalinity contributes to scale formation, because it encourages deposition of calcium carbonate. In natural waters, the alkalinity almost always consists of bicarbonate, although some carbonate alkalinity may also be present. Borate, hydroxide, phosphate, and other constituents, if present, are included in the alkalinity measurement in treated waters.

Alkalinity is measured using two different end-point indicators. The **phenolphthalein alkalinity (P alkalinity)** measures the strong alkali present, and the **methyl orange alkalinity (M alkalinity)**, or **total alkalinity**, measures the total alkalinity in the water. Note that the total alkalinity includes the phenolphthalein alkalinity. For most natural waters, the actual chemical species present can be estimated from the two alkalinity measurements. Treated waters include the hydroxide alkalinity contributed by OH^- (Table 1).

pH is a measure of the concentration of hydrogen ions, or the acid strength, of a solution. It is the negative logarithm of the hydrogen ion concentration (pH 1, very acidic; pH 14, very basic; pH 7, neutral at ambient temperature.) The pH concept is fundamental to an understanding of water chemistry and to control of pretreatment systems, boilers, and cooling towers. All of these systems depend on either precise pH control or on maintaining the pH above a specified

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Table 1 Alkalinity Relationship Based on P and M Tests

Situation	Level of Alkalinity		
	Hydroxyl	Contributed by Carbonate	Bicarbonate
P = M	M	0	0
P > 1/2M	2P - M	2(M - P)	0
P = 1/2M	0	M	0
P < 1/2M	0	2P	M - 2P
P = 0	0	0	M

P = P alkalinity = phenolphthalein alkalinity

M = M alkalinity = methyl orange (total) alkalinity

minimum level. Unexpected changes in pH are usually a warning of problems that must be corrected.

Chlorides are the total of dissolved chloride salts of sodium, potassium, calcium, and magnesium present in water. Sodium chloride (common salt, NaCl), and calcium chloride (CaCl₂) are the most common of the chloride salts found in water. Chlorides do not ordinarily contribute to scale, because they are very soluble. However, chlorides are corrosive and cause excessive corrosion when present in high concentration, as in seawater, because of their conductivity and because the small size of the chloride ion permits the continuous flow of corrosion current when surface films are porous. The amount of chlorides in water is a useful measuring tool in evaporative systems for determining cycles of concentration. Most water constituents change (increase or decrease) when common treatment chemicals are added or because of chemical changes that take place in normal operation. With few exceptions, only evaporation affects chloride concentrations, so the ratio of chlorides in a water sample from an operating system to those of the makeup water provides a measure of how much the water has been concentrated. (*Note:* Chloride levels will change if the system is chlorinated.)

Conductivity or **specific conductance** measures the ability of water to conduct an electrical current electricity or be an electrolyte. Conductivity increases with increasing total dissolved solids (ions) present in the water. Specific conductance can be used to estimate total dissolved solids.

Dissolved solids consist of salts and other materials that combine with water as a solution. They can affect the formation of corrosion and scale. Low-solids waters are generally corrosive because they have less tendency to deposit protective scale. If a high-solids water is nonscaling, it tends to produce more intensive corrosion because of its high conductivity. Total dissolved solids are referred to as **TDS**.

Suspended solids include both organic and inorganic solids suspended in water (particularly unpurified water from surface sources or those that have been circulating in open equipment). Organic matter in surface supplies may be colloidal. Naturally occurring compounds such as lignins and tannins are often colloidal. At high velocities, hard suspended particles can abrade equipment. Settled suspended matter of all types can contribute to corrosion. Total suspended solids are referred to as **TSS**.

Silica is dissolved sand or silica-bearing rock (such as quartz) through which the water flows. Silica is the cause of very hard and tenacious scales that can form in heat transfer systems. These deposits can be particularly hard to remove if allowed to concentrate. Fortunately, silicate deposition is less likely than other deposits.

Soluble iron in water can originate from metal corrosion in water systems or as a contaminant in the makeup water supply. The iron can form heat-insulating deposits by precipitation as iron hydroxide or iron phosphate in the presence of phosphate-based water treatment or phosphate in the makeup water.

Sulfates are the dissolved sulfate salts of sodium, potassium, calcium, and magnesium in the water. They are present because of the dissolution of sulfate-bearing rock, such as gypsum. Calcium

and magnesium sulfate scale is very hard and difficult to remove and greatly interferes with heat transfer. Sulfates also contribute to scale formation in high-calcium waters. Calcium sulfate scale, however, forms at much higher concentrations than the more common calcium carbonate scale. High sulfates also contribute to increased corrosion because of their high conductivity and support of **microbiologically influenced corrosion (MIC)**.

Turbidity can be interpreted as a lack of clarity or brilliance in a water. It should not be confused with color. A water may be dark in color but still clear and not turbid. Turbidity is caused by suspended matter, in a finely divided state, that can scatter and deflect incoming light. Clay, silt, organic matter, microscopic organisms, and similar materials are contributing causes of turbidity. Although suspended matter and turbidity are closely related, they are not synonymous. Suspended matter is the quantity of insoluble material in water that can be removed by filtration. Turbidity is the amount of opacity caused by suspended matter. Turbidity of water used in HVAC systems should be as low as possible. This is particularly true for boiler feedwater. The turbidity can concentrate in the boiler and settle out as sludge or mud and lead to deposition. It can also cause increased boiler blowdown, plugging, overheating, priming, and foaming.

Biological matter such as bacteria, algae, and fungi can be present in water and their growth in water systems can cause operating, maintenance, and health problems. Microbial growth can occur in most water systems below 65°C. Problems caused by biological materials range from green algae growth in cooling towers to bacterial slime formations. This growth can plug equipment where flow is essential, drastically reduce heat exchanger (transfer) efficiencies, and also cause microbial corrosion.

2. ALTERNATIVE WATER SOURCES

This section is based on Browning and Weimar (2011).

Facilities are under continuous pressure to reduce costs and operate in a more environmentally responsible manner. Historically, energy conservation has overshadowed water conservation in these efforts. However, in many locations, the reduced availability and increased cost of water now make water conservation a much more attractive target. More facilities are subject to limits on water consumption and the amount of wastewater that can be discharged. Although there are energy source alternatives to oil and gas, there is no such substitute for water. The economic and environmental payback on reducing water usage is greater than ever.

As a large consumer of potable water, evaporative-cooling-water systems, including cooling towers, are an obvious target for water conservation efforts. Because of supply and cost pressures, more facilities are considering alternative makeup water sources, such as air handler condensate, rainwater, and reclaim water. In some cases, alternative water sources are being blended with potable water to improve water use efficiency. Using one or more of these alternative water sources for cooling tower makeup conserves fresh water for other uses and can provide significant cost savings.

Evaluating an Alternative Water Source

It is important to understand the impurities in an alternative makeup water source and how they will affect cooling tower operation before substituting for potable water. Some water sources can be successfully used without further treatment, whereas others require additional treatment measures to control problems related to corrosion, scale, and microbiological growth. An engineering and economic analysis is necessary to determine both the feasibility and potential cost savings. In general, the higher the cost and poorer the quality of the potable water source, the better the payback associated with using an alternative source. As with any water conservation product, water meters are essential to monitor water usage and benchmark improvements.

Air Handler Condensate. In warm, humid climates, the normal operation of air-conditioning equipment produces large quantities of condensate from the air handler cooling coils. This cold, near-distilled-quality water is typically sent to the drain. In some cases, this water can be readily recovered for other uses, including cooling tower makeup. Because air handler condensate does not contain the dissolved mineral impurities present in potable water, using this cold, nearly pure water for cooling tower makeup also allows operation at lower bleed rates.

Because the quantity of condensate generated by a cooling coil is a direct function of the airflow rate and change in the relative humidity, it will vary considerably throughout the year. In some locations, the amount can be staggering. For example, a 3500 kW cooling load in a commercial facility with 25% outdoor air produces 0.30 L/s of condensate when the outdoor air temperature is 29°C with 80% rh and 0.17 L/s with 60% rh. Case studies have shown that 10% to 40% of cooling tower makeup requirements can often be met with air handler condensate in facilities that operate in warm, humid climates (e.g., Florida, Georgia, Alabama, Mississippi, Louisiana, east Texas, and along the east coast of the United States).

Depending on the location of the air-handling units and the cooling towers, the collection system can be as simple as a gravity-fed tank with a level controller and pump. Corrosion-resistant tanks and piping are recommended because of the corrosivity of such pure water. Typically, an oxidizing biocide is added to the condensate storage tank to prevent microbiological problems. Each facility is different, but the water savings and payback on using air handler condensate for cooling tower makeup water can be very significant.

Rainwater. Although unpredictable, rainwater is a good alternative in some areas. Approximately 1 L of water can be recovered per millimetre of rain per square metre of collection surface. For a 200 m² roof, this translates to more than 200 L of water per mm of rain.

A typical rainwater recovery system directs rainwater from the roof to a storage tank rather than a storm sewer. This cache of water can then be used for various purposes throughout a facility, including irrigation and cooling tower makeup water. Parking decks can also be used to harvest rainwater. However, special media filters are required, to remove oil and other contaminants before use.

Like air handler condensate, rainwater is relatively pure. Once collected from a roof and filtered for contaminants, it can be used as cooling tower makeup water with little treatment other than the addition of an oxidizing biocide to the storage tank to minimize microbiological growth.

Reclaimed Water. Reclaimed water, or recycled water, is highly treated wastewater from a municipal wastewater treatment plant. This nonpotable water source is delivered to a facility in purple- or lavender-colored piping to distinguish it from potable water supplies. It is suitable for irrigation, deep well injection, and possibly for open recirculating cooling systems.

Compared to potable water, reclaim water contains a higher concentration of hardness and alkalinity, which increases the tendency to form calcium carbonate scale deposits. It can also contain appreciable levels of phosphate and ammonia, components not normally present in significant amounts in potable water.

The increased phosphate content in reclaimed water also makes calcium phosphate scale formation in heat exchange equipment a concern, unless the proper treatment measures are taken. These measures may include operating the cooling tower at a higher bleed rate, using sulfuric acid for pH control, and/or adding a phosphate-specific polymeric dispersant.

Although reclaimed water is disinfected to control pathogenic microorganisms, there is an increased potential for microbiological problems when used in cooling tower systems. In part, this is related to the presence of ammonia and other nitrogen compounds, which are nutrients that support bacteria growth. Reclaimed water also has higher background bacteria levels than potable water. Because of

the increased potential for corrosion and deposit problems related to bacteria growth, additional biocides are usually required. A combination of oxidizing and nonoxidizing biocides usually works best. Because of its unique properties, chlorine dioxide is often an excellent biocide for this application. It is a selective oxidizing biocide that can provide effective microbiological control at low levels. New technologies greatly simplify chlorine dioxide generation and application, making this an attractive alternative biocide.

Blended Water. Blending one or more alternative water sources can also reduce overall water consumption and costs associated with operating a cooling tower system. In some applications, it may be necessary to blend potable water with reclaim water to provide a makeup water quality suitable for use in cooling towers. Where there is excess water softener or reverse osmosis (RO) capacity, blending with high-alkalinity, high-hardness potable water can allow a cooling tower to operate at greatly reduced bleed rates. Alternative water streams such as RO reject water may also be suitable for use as tower makeup with blending.

Consistent blending is important when considering a blended-water supply for cooling tower makeup. It is difficult to control the bleed rate and treatment levels when the makeup quality varies widely. Equipment systems can be engineered to accurately blend two or more water supplies.

Evaluating Alternative Water Options

An engineering and economic evaluation is necessary to determine the feasibility and benefits associated with using alternative water sources in cooling-water systems. Because each building is different, a water treatment professional should be involved in the evaluation to ensure that the cooling-water systems operate reliably and efficiently. In general, air handler condensate and rainwater can be readily used where available. Using reclaimed or blended water requires more in-depth analysis and is generally not recommended without effective on-site water treatment monitoring.

3. DEPOSITION, SCALE, AND SUSPENDED-SOLIDS CONTROL

Several different types of deposits can form in boiler and cooling-water systems, and terms such as scale, fouling, deposit, film, coating, precipitate, and others are sometimes used interchangeably in the industry to describe these materials. However, it is important to use the correct term in describing these phenomena, because the operating procedures and chemical treatments used to help prevent these various deposits from forming, and to remove them when necessary, depend on the specific composition of the deposits.

Deposit refers to any material formed on either the internal or external surfaces of components in contact with water.

Fouling describes the condition of a system in which deposits have formed, including microbiological fouling.

Scale is formed from minerals, formerly dissolved in water, deposited from the water onto heat transfer surfaces or in-flow water lines. As water is evaporated in a cooling tower, the concentration of dissolved solids becomes greater, and the solubility of particular scale-causing mineral salts can be exceeded. When this situation occurs in an untreated cooling-water system, scale will form on any surface in contact with the water, especially on heat transfer surfaces. The most common scaling minerals are (1) calcium carbonate, (2) calcium phosphate, (3) calcium sulfate, and (4) silica, usually in that order. Formation of magnesium silicate scale is also possible under certain conditions. Most salts, including silica, are more soluble in hot water than in cold water; however, most calcium and magnesium salts, including calcium phosphate and calcium carbonate, are more soluble in cold water. This is called **reverse solubility**. As recirculating water passes through the cooling system, the water temperature increases. As a result, calcium and magnesium scales may

form anywhere in the system, but most likely on heated surfaces such as heat exchangers or surface condensers. Silica forms in areas having the lowest water temperature, such as in the cooling tower fill.

Minerals such as calcium and magnesium are relatively insoluble in water and can form scale deposits when exposed to conditions commonly found in cooling-water systems. A layer of scale as thin as 0.4 mm can reduce heat exchanger efficiency by 15%. Scale formation is controlled in cooling-water systems by scale inhibitors, such as threshold inhibition chemicals and scale conditioners. Scale- and deposit-control water treatment programs include polymers, phosphonates, and polyphosphates that prevent scale formation by keeping the scale-forming minerals in solution to prevent deposits from forming.

Several key factors influence whether scale forms:

- Temperature
- pH
- Alkalinity
- Hardness (amount of scale-forming salts)
- Total dissolved solids (influence of other dissolved materials, which may or may not be scale-forming)

As any of these factors changes, scaling tendencies also change. Changes in pH or alkalinity can greatly affect scale formation. For example, as pH or alkalinity increases, calcium carbonate, a common scale constituent in cooling systems, becomes less soluble and deposits on surfaces.

Some materials, such as silica (SiO_2), are less soluble at lower alkalinities. When the amount of scale-forming material dissolved in water exceeds its saturation point, scale may result. In addition, other dissolved solids may influence scale-forming tendencies. In general, a higher level of scale-forming dissolved solids results in a greater chance for scale formation.

Scaling Indices

To aid in the determination of the tendency of water to form or dissolve calcium carbonate scale, several scaling indices have been developed to describe the condition of water based on the properties of the bulk water. These indices are only for predicting calcium carbonate scale, not scale of other calcium salts. The indices are calculated using the pH, alkalinity, calcium hardness, temperature, and total dissolved solids of the water.

Langelier Saturation Index (LSI). In 1936, this index was developed to calculate the calcium carbonate scale-forming and scale-dissolving tendencies of drinking (potable) water at or near ambient temperatures (Langelier 1936). Using a water's calcium hardness, total alkalinity, and total dissolved solids measurements along with the water's pH and temperature values, the pH of saturation, $\text{pH}(s)$, is calculated from a logarithmic-based formula. Subtracting the water's $\text{pH}(s)$ from its actual pH then results in the LSI. If the water's measured pH, $\text{pH}(\text{actual})$, is greater than its $\text{pH}(s)$, thus resulting in a positive LSI value, the water has a scale-forming tendency. If the water's $\text{pH}(\text{actual})$ is less than its $\text{pH}(s)$, thus resulting in a negative LSI value, the water will have a scale-dissolving tendency. The water's equilibrium or neutral value is at an LSI of zero. Because this index was originally designed to predict calcium carbonate scale in potable water, there are serious deficiencies in the accuracy of this index when applied to evaporative cooling-water systems.

The temperature component in the LSI calculation is considered appropriate for potable water that is carried at ambient soil temperatures through buried distribution piping. However, this was later deemed insufficient for process water used for cooling towers or boilers where values tended almost always to be positive, yet indications of deposition of calcium carbonate were absent. Experience has dictated that the LSI can be used as a trending value in process

water systems to indicate changes in stability, rather than an absolute condition.

The LSI is calculated as

$$\text{LSI} = \text{pH}(\text{actual}) - \text{pH}(s)$$

where

$$\text{pH}(s) = (9.3 + A + B) - (C + D)$$

$$A = (\log[\text{TDS}] - 1) / 10$$

$$B = -13.12 \times \log(\text{temp } ^\circ\text{C} + 273) + 34.55$$

$$C = \log[\text{Ca}^{2+}] - 0.4$$

$$D = \log[\text{alkalinity}]$$

Note: All log values are base 10; alkalinity is the total alkalinity measured as ppm CaCO_3 ; Ca^{2+} is the calcium measured as ppm CaCO_3 ; and TDS is total dissolved solids measured in ppm.

Ryznar Stability Index (RSI). This index is a more sensitive formula for predicting calcium carbonate scale (Ryznar 1944). Ryznar altered the LSI by measuring scale thickness in distributed water systems and comparing the calculated LSI with field results. With this information, he made revisions to the LSI. With his formula, $2 \times \text{pH}(s) - \text{pH}(\text{actual})$, an RSI value of 6.0 is considered neutral water, with values > 6.0 indicating a tendency to dissolve calcium carbonate, and values < 6.0 a tendency to deposit calcium carbonate. Ryznar's index gave more accurate results versus the LSI in waters with a pH less than 7.8, but would still give an indication of scale formation at higher pH values. Regardless, the RSI was useful for the era's acid feed water treatment programs, which operated at $\text{pH} < 7.8$.

The RSI is calculated as

$$\text{RSI} = 2 \times \text{pH}(s) - \text{pH}(\text{actual})$$

where $\text{pH}(s)$ is calculated as in the LSI.

Practical (Puckorius) Scaling Index (PSI). Puckorius and Brooke (1991) presented a modified version of the RSI that gives a more accurate and consistent indication of the calcium carbonate scaling potential of cooling water. The PSI takes into consideration the effect of the type of total alkalinity of the cooling water on the measured pH, $\text{pH}(\text{actual})$. The measured pH does not always relate correctly to bicarbonate alkalinity, because of the buffering effect of other ions. Rather than using the measured pH in calculating the PSI, an adjusted or equilibrium pH, $\text{pH}(\text{eq})$, is used. As with the RSI, a PSI value of 6 indicates stable water, and a value lower than 6 indicates a scale-forming tendency. Without scale control treatment, a cooling tower with a PSI of 6 to 7 should operate scale free. However, a PSI of less than 6 indicates that scaling may occur. Use of the PSI is most applicable when cooling-water pH is above 7.5.

The PSI is calculated as

$$\text{PSI} = 2 \times \text{pH}(s) - \text{pH}(\text{eq})$$

where $\text{pH}(s)$ is as calculated in the LSI, and $\text{pH}(\text{eq}) = 1.465 \times \log[\text{alkalinity as } \text{CaCO}_3] + 4.54$.

Simple models and calculators along with more information on these indices can be found online from various sources.

Scale and Deposit Formation Control

Methods used to control scale and deposit formation include the following:

- Limit the concentration of scale-forming minerals, impurities, and contaminants in a boiler or evaporative-cooling-water system by intentionally "wasting" (removing) water from the system via blowdown (bleedoff). This, in effect, lowers concentration that tends to increase during the continuing evaporation of steam or cooling water from these systems. Scale control is thus achieved through operation of the system at subsaturated conditions.

- Remove scale-forming minerals, impurities and contaminants before they enter the boiler or cooling-water system, using external or pretreatment systems. This can be done using (1) softened water, blending soft or RO water with other makeup water to achieve a desired saturation index, (2) cycles of concentration, or (3) both methods.
- Effect mechanical changes in the system, such as increasing water flow or surface areas of heat exchangers, to reduce tendencies and potential for scale/deposit formation.
- Feed acid to reduce alkalinity and keep common scale-forming minerals such as calcium carbonate in solution.
- Implement a water treatment program designed to control scale and deposit formations in the boiler or cooling-water system.

Controlling cycles of concentration also controls the time that minerals, as well as treatment chemicals and other water constituents, are held within a system. Evaporative-cooling-water systems have a load- and volume-dependent water residence or turnover time referred to as the **holding time index (HTI)**, also called the **half-life** or **retention time** of the system. HTI is the measure of time that it takes for an analyte in the cooling-water system to decrease to 50% of its original value through the process of system losses (blowdown and drift) plus the addition of makeup water to the system. The greater the HTI (half-life) of the system, the longer water is held in the system and the greater the probability that dissolved, scale-forming minerals will nucleate to produce deposits. At the same time, the greater the HTI (half-life) of the system, the longer a biocide dosage is held in the system water for a greater contact time to promote microbial kill or control.

HTI for a cooling-water system is calculated as follows:

$$\text{HTI} = 0.693 \times V/\text{BD}$$

where

V = volume of system

BD = blowdown rate for system \approx evaporation rate (ER)/[cycles of concentration (CC) - 1]

Water treatment chemical scale inhibitors work by the following mechanisms:

- **Threshold inhibition chemicals** control scale formation by dramatically extending the time required for deposit nucleation. When nucleation time is extended beyond a system's HTI, mineral deposits fail to form. The most commonly used threshold scale inhibitors are organophosphorus compounds (phosphonates) and low-molecular-weight acrylate polymers. Both classes of materials function as threshold inhibitors; however, the polymeric materials are more effective as dispersants.
- **Scale conditioners** modify the crystal structure of scale forming minerals as the nucleate, creating a bulky, transportable sludge instead of a hard deposit. Scale conditioners include lignins, tannins, and polymeric compounds.

Suspended Solids and Deposition Control

Strainers, filters, and separators may be used to reduce suspended solids to an acceptable low level. Generally, if the screen is 200 mesh, with an aperture of 74 μm , it is called a strainer; if it is finer than 200 mesh, it is called a filter.

Strainers. A strainer is a closed vessel with a cleanable screen designed to remove and retain foreign particles down to 25 μm diameter from various flowing fluids. Strainers extract material that is not wanted in the fluid to protect equipment downstream from constrictions, and allow saving the extracted product if it is valuable. Strainers are available as single-basket or duplex units, manual or automatic cleaning units, and may be made of cast iron, bronze, stainless steel, copper-nickel alloys, or plastic. Magnetic inserts are available where microscopic iron or steel particles are present in the fluid.

Cartridge Filters. These are typically used as final or tertiary filters to remove nearly all suspended particles from about 100 μm down to 1 μm or less. Cartridge filters are typically disposable (i.e., once plugged, they must be replaced). The frequency of replacement, and thus the economical feasibility of their use, depends on the concentration of suspended solids in the fluid, the size of the smallest particles to be removed, and the removal efficiency of the cartridge filter selected.

In general, cartridge filters are favored in systems where contamination levels are less than 0.01% by mass (< 100 mg/kg). They are available in many different materials of construction and configurations. Filter media materials include yarns, felts, papers, non-woven materials, resin-bonded fabric, woven wire cloths, sintered metal, and ceramic structures. The standard configuration is a cylinder with an overall length of approximately 250 mm, an outside diameter of approximately 65 to 70 mm, and an inside diameter of about 25 to 40 mm, where the filtered fluid collects in the perforated internal core. Overall lengths from 0.1 to 1 m are readily available.

Cartridges made of yarns, resin-bonded, or melt-blown fibers normally have a structure that increases in density towards the center. These depth-type filters capture particles throughout the total media thickness. Thin media, such as pleated paper (membrane types), have a narrow pore size distribution design to capture particles at or near the surface of the filter. Surface-type filters can normally handle higher flow rates and provide higher removal efficiency than equivalent depth filters. Cartridge filters are rated according to manufacturers' guidelines. Surface-type filters have an absolute rating, whereas depth-type filters have a nominal rating that reflects their general classification function. Higher-efficiency, melt-blown depth filters are available with absolute ratings as needed.

Bag-Type Filters. A type of cartridge filter, these filters are composed of a bag of mesh or felt supported by a removable perforated metal basket, placed in a closed housing with an inlet and outlet. The housing is a welded, tubular pressure vessel with a hinged cover or a clamped cover on top for access to the bag and basket. Housings are made of carbon or stainless steel. The inlet can be in the cover, in the side (above the bag), or in the bottom (and internally piped to the bag). The side inlet is the simplest type. In any case, the liquid enters the top of the bag. The outlet is located at the bottom of the side (below the bag). Pipe connections can be threaded or flanged. Single-basket housings can handle up to 14 L/s, multibaskets up to 220 L/s.

The support basket is usually of 304 stainless steel perforated with 3 mm holes. (Heavy wire mesh baskets also exist.) The baskets can be lined with fine wire mesh and used by themselves as strainers, without adding a filter bag. Some manufacturers offer a second, inner basket (and bag) that fits inside the primary basket. This provides for two-stage filtering: first a coarse filtering stage, then a finer one. The benefits are longer service time and possible elimination of a second housing to accomplish the same function.

Filter bags are made of many materials: cotton, nylon, polypropylene, and polyester, with a range of size ratings from <1 to 825 microns (0.001 to 0.825 mm). Most common are felted materials because of their depth-filtering quality, which provides high dirt-loading capability, and their fine pores. Mesh bags are generally coarser, but are reusable and, therefore, less costly. The bags have a support ring sewn into their opening; this holds the bag open and seats it on top of the basket rim. They can be configured with lift handles, thermal-sealed edges instead of sewn stitches, and glazed (thermal-pressed) finish to prevent release of fibers. Filtration efficiency of these bags ranges from 50 to 97%, depending on the fabric configurations. In operation, the liquid enters the bag from above, flows out through the basket, and exits the housing cleaned of particulate down to the desired size. The contaminant is trapped inside the bag, making it easy to remove without spilling any downstream.

Sand Filters. A downflow filter is used to remove suspended solids from a water stream. The degree of suspended solids removal depends on the combinations and grades of the medium being used in the vessel. During the filtration mode, water enters the top of the filter vessel. After passing through a flow impingement plate, it enters the quiescent (calm) freeboard area above the medium.

In multimedia downflow vessels, various grain sizes and types of media are used to filter the water. This design increases the suspended solids holding capacity of the system, which in turn increases the backwashing interval. Multimedia vessels might also be used for low-suspended-solids applications, where chemical additives are required. In the multimedia vessel, the fluid enters the top layer of anthracite media, which has an effective size of 1 mm. This relatively coarse layer removes the larger suspended particles, a substantial portion of the smaller particles, and small quantities of free oil. Flow continues down through the next layer of fine garnet material, which has an effective size of 0.3 mm. A more finely divided range of suspended solids is removed in this polishing layer. The fluid continues into the final layer, a coarse garnet material that has an effective size of 2 mm. Contained in this layer is the header/lateral assembly that collects the filtered water.

Sand filters for cooling-water systems are usually high rate [$49 \text{ m}^3/(\text{h} \cdot \text{m}^2)$] with filter media rated from 0.45 to 10 microns (0.0045 to 0.01 mm). Some filter vessels are configured to allow water to enter at an angle to create a vortex-shaped filter bed to enhance removal efficiency. Total filtration rate is determined by either system volume turnovers or percent of circulation flow rate. They are usually installed sidestream with a booster pump. When they are installed next to cooling towers, filter piping is used to sweep clean tower basin floors at a rate of 2.44 to 3.67 $\text{m}^3/(\text{h} \cdot \text{m}^2)$ via sweep nozzles. This usually calls for a bigger booster pump to create the sweeping action.

When the vessel has retained enough suspended solids to develop a substantial pressure drop, the unit must be backwashed either manually or automatically by reversing the direction of flow. This operation removes the accumulated solids out through the top of the vessel.

Centrifugal-Gravity Separators. In this type of separator, liquids containing solids enter the unit tangentially, which sets up a circular cyclone flow path. The liquids are accelerated into the separation chamber. Centrifugal forces toss the particles heavier than the liquid to the perimeter of the separation chamber. Solids gently drop along the perimeter and into the quiescent collection chamber of the separator. A low-solids liquid is then drawn into the separator vessel vortex (low-pressure area) and up through the separator outlet at the top of the vessel. Solids are either purged periodically by either a manual or automatic timed purge, or continuously bled from the separator to a solids collection/filter chamber. Advantages of separators include a constant pressure drop even as solids are collected, a negligible water loss in the purge cycle, and no backwash or interruption of service.

Special Methods. Localized areas frequently can be protected by special methods. Thus, pump-packing glands or mechanical shaft seals can be protected by fresh water makeup to the seals or by circulating water from the pump casing through a cyclone separator or filter, then into the lubricating chamber. In smaller equipment, a good dirt-control measure is to install backflush connections and shutoff valves on all condensers and heat exchangers so that accumulated settled dirt can be removed by backflushing with makeup water or detergent solutions. These connections can also be used for acid cleaning to remove calcium carbonate scale.

In specifying filtration systems, third-party testing by a qualified university or private test agency should be requested. The test report documentation should include a description of methods, piping diagrams, performance data, and certification.

Filters described in this section may also be used where industrial process cooling water is involved. For this type of service,

consultation with the filtration equipment manufacturer is essential to ensure proper application.

4. CORROSION AND CORROSION CONTROL

Corrosion is the destruction of a metal or alloy by chemical or electrochemical reaction with its environment. It is the mechanism by which a metal reverts back to its natural state, a metal ore. In most instances, this reaction is electrochemical in nature, much like that in an electric battery. For corrosion to occur, a corrosion cell consisting of an anode, a cathode, an electrolyte, and an electrical connection must exist. Metal ions dissolve into the electrolyte (water) at the anode, leaving behind electrons. These electrons flow through the metal (electric connection) to other points (cathodes) where electron-consuming reactions occur. The result of this activity is the loss of metal and often the formation of a deposit. The rapidity of the corrosion depends upon the rate of flow of the electrons. Mechanisms for various types of corrosion are shown in Figure 1.

Types of Corrosion

Corrosion is often divided into three broad categories: (1) uniform corrosion, referred to as general corrosion; (2) localized corrosion, also called pitting corrosion; and (3) galvanic corrosion, also known as dissimilar metal corrosion. Many other types of corrosion associated with these three main categories are of water treatment concern and commonly encountered in boiler and cooling water systems for both HVAC and processes. These include stress, fatigue, crevice, erosion, and microbiologically influenced corrosion.

Uniform or general corrosion (Figure 1D) is the most common type of corrosion and is caused by a chemical or electrochemical reaction that results in the deterioration of the entire exposed surface of a metal. Ultimately, the metal can deteriorate to the point of failure. Uniform attack corrosion accounts for the greatest amount of metal destruction by corrosion, but is considered a normal condition when metals are exposed to water-based fluids, because it is (1) evenly distributed over a given metal surface throughout a system and (2) predictable, manageable, and often preventable. Uniform corrosion can be compensated for by (1) using corrosion-resistant construction materials, (2) applying protective coatings, or (3) providing appropriate cathodic corrosion protection. Additionally, the effects of uniform corrosion can be anticipated through measurement of material specimens exposed to the anticipated operating environment at a corrosion coupon rack. Coupons are inserted in the rack for a predetermined exposure before being removed, cleaned, weighed, and examined to determine rates of corrosion. By altering construction materials of systems in fabrication or construction and by evaluating treatment methods of operating systems, adequate control of uniform corrosion can be accomplished.

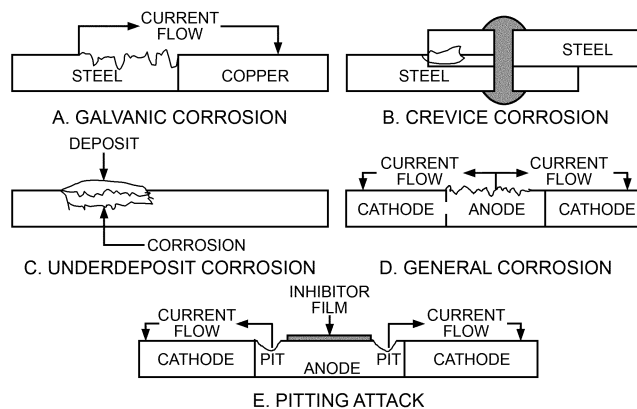


Fig. 1 Corrosion Types and Mechanisms

General corrosion is found in various forms in heat transfer equipment. In a condenser water or cooling tower water circuit, it can be seen as an overall deterioration of the metal surface, with an accumulation of rust and corrosion products in the piping and water boxes. On copper condenser tubes, it is observed most frequently as a surface gouging or a uniform thinning of the tube metal. In boilers, general corrosion is observed in the total overall disintegration of the tube metal surface in contact with the boiler water.

General corrosion occurs over the entire surface of the metal, resulting in a uniform loss of metal rather than a localized type of attack. It is often, but not always, accompanied by an accumulation of corrosion products over the surface of the metal. Iron and other metals are corroded by electrochemical reaction, resulting in the metal going into solution in the water. It is necessary, then, to limit corrosion of these metals by reducing the activity of both hydroxyl ions and hydrogen ions and maintaining a neutral environment. Another important factor in the corrosion process is dissolved oxygen. The evolution of hydrogen gas in these reactions tends to slow the rate of the corrosion reaction and, in many instances, stop it altogether by forming an inhibiting film on the surface of the metal; this film physically protects the metal from the water.

Accumulation of rust and corrosion products is further promoted by the presence of dissolved oxygen. Oxygen reacts with the dissolved metal, eventually forming the oxide, which is insoluble and, in the case of iron, builds up a voluminous deposit of rust. Because the role of dissolved oxygen in the corrosion process is important, removal of dissolved oxygen is an effective procedure in preventing corrosion in closed systems.

Localized or pitting corrosion (Figure 1E) results when a small hole or pit forms in the metal surface, usually as the result of inconsistent inhibitor film formation at that location. This area becomes anodic, while part of the remaining metal becomes cathodic, producing a localized galvanic reaction, often referred to as a **concentration cell**. The deterioration of this small area penetrates the metal and can quickly lead to failure. This form of corrosion is often difficult to detect because it is usually relatively small and may be covered and hidden by corrosion-produced compounds (corrosion by-products). Pitting is the most serious form of corrosion, because the action is concentrated in a small area. Pits often appear with depth and diameter roughly singular in ratio. Continued corrosion reaction in pits of ferrous metals can cause the appearance of hollow, tube-like growths above the metal surface, called **tubercles**. These are formed by layering deposits of iron oxide species, a by-product of the pit formation at the base of the tubercle. Like corrosion cells, pits may reach an autocatalytic stage of rapid corrosion, though not always. Tubercles, however, are always the result of an autocatalytic process. Unlike crevice corrosion, pitting is thought to be self-initiated in otherwise unmarred surfaces by the presence of deposits and chloride salts. The pit then concentrates chlorides in the hollow. The process is further accelerated by the presence of oxygen, which creates a localized adjacent cathode to the anodic surface of the pit itself, forcing concentrated anodic deterioration and enlarging the pit.

Galvanic corrosion or dissimilar metal corrosion (see Figures 1A and 2), occurs when two different metals are located together in a corrosive electrolyte (solution). A galvanic couple forms between the two metals, where one metal becomes the anode and the other the cathode. The anode, or sacrificial metal, corrodes and deteriorates faster than it would alone, while the cathode deteriorates more slowly than it would otherwise. Three conditions must exist for galvanic corrosion to occur:

- Electrochemically dissimilar metals must be present
- The metals must be in electrical contact
- The metals must be exposed to an electrolyte

Common examples of galvanic corrosion in water systems are metal-to-metal contacts between steel and copper alloys (brass),

aluminum and steel, zinc and steel, and galvanized steel and steel. If galvanic corrosion occurs, the metal named first is the anode and experiences the corrosion.

Stress corrosion cracking (SCC) or **environmental cracking** can result from a combination of environmental conditions affecting the metal and in alloys subject to tensile stress. The stress may be either applied, residual (from processing), or a combination. The resulting crack formation is generally intergranular. Chemical-, temperature-, and stress-related conditions can result in the following types of environmental corrosion:

- Stress corrosion cracking
- Corrosion fatigue
- Hydrogen-induced cracking
- Liquid metal embrittlement

Corrosion fatigue may occur by one of two mechanisms. In the first, cyclic stresses (e.g., from rapid heating and cooling) are concentrated at points where surface defects are present and corrosion has roughened or pitted the metal surface. In the second type, cracks often initiate because of the action of applied cyclic stresses where metal surfaces are covered by a magnetite film.

Caustic cracking occurs when metal is stressed in a fluid with a high caustic (high pH) content, and a mechanism of concentration occurs.

Crevice corrosion (see Figure 1) occurs in the void between a metal and another surface. These opposing surfaces can be metal (similar or dissimilar), gaskets, organic residue, or scale deposits. In this void, and usually in the presence of a stagnant solution, a localized corrosion environment is created. Also referred to as **under-deposit corrosion**, it exhibits similar corrosion processes found in a concentration cell corrosion model. As in pitting, the crevice allows the concentration of chlorides in the void, and the presence of oxygen enhances the reaction.

Erosion corrosion (flow-accelerated corrosion) occurs as a result of flow or impact that can physically remove inhibitor films and the protective metal oxide surface. This type of corrosion usually occurs because of altered flow patterns or a flow rate that is above design. Suspended solids in a solution can greatly contribute to erosion corrosion. Control of suspended solids can reduce erosion in systems and enhance material life cycle and durability. **Cavitation corrosion**, a form of erosion corrosion, is caused by the rapid formation and collapse of vapor bubbles during a change in fluid pressures in a solution and adjacent to a metal surface.

Microbiologically influenced corrosion (MIC), also called **microbial corrosion**, **bacterial corrosion**, or **biocorrosion**, involves the reaction of microbiological species with metals. It is

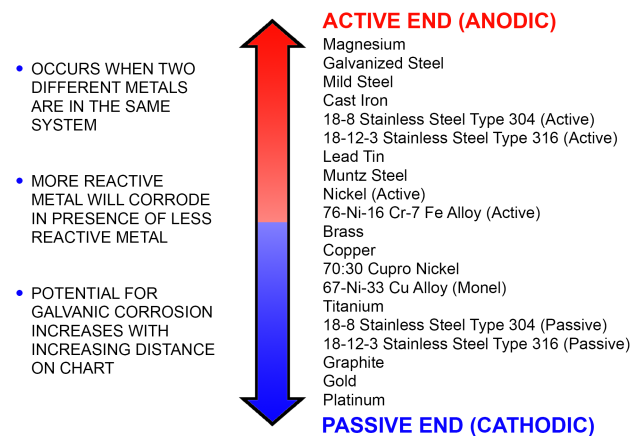


Fig. 2 Galvanic Corrosion

Table 2 Corrosion Rate Guidelines

Open Recirculating HVAC Cooling-Water Systems			
Description	Carbon Steel	Copper Alloys	Stainless Steel*
Negligible or excellent	≤0.0254 mm	≤0.00254 mm	Acceptable <0.00254 mm
Mild or very good	0.0254 to 0.0762 mm	0.00254 to 0.00635 mm	Unacceptable >0.00254 mm
Good	0.0762 to 0.127 mm	0.00635 to 0.00889 mm	—
Moderate to fair	0.127 to 0.2032 mm	0.00889 to 0.0127 mm	—
Poor	0.2032 to 0.254 mm	0.0127 to 0.0254 mm	—
Very poor to severe	>0.254 mm	>0.0254 mm	—
Closed Recirculating HVAC Water Systems (Hot, Chilled, and Tempered Loops)			
Description	Carbon Steel	Copper Alloys	Aluminum*
Excellent	≤0.00508 mm	≤0.00254 mm	<0.00127 mm
Good	0.00508 to 0.0127 mm	0.00254 to 0.00889 mm	0.00127 to 0.00254 mm
Moderate	0.0127 to 0.02032 mm	0.00635 to 0.00889 mm	0.00254 to 0.00508 mm
Poor	0.02032 to 0.0254 mm	0.00635 to 0.0127 mm	0.00508 to 0.00762 mm
Very poor to severe	≥0.0254 mm	≥0.0127 mm	>0.00762 mm

Source: Boffardi (2000).

*Not an AWT Guideline

caused or promoted by microorganisms, usually chemoautotrophs, which are microbes that can produce corrosive acids as a part of their cellular metabolism on the metal surface. MIC can be a very serious problem in building HVAC recirculating water systems, involving many forms and mechanisms and many types of micro-biological organisms, including the following:

- **Iron-related bacteria (IRB)**, such as *Gallionella ferrugine* and *Ferrobacillus* species, cause corrosion of iron and steel in recirculating water systems by direct metabolism of iron. Some of these organisms consume iron as a part of their metabolic process and then deposit it in the form of hydrated ferric hydroxide along with mucous secretions. Iron bacteria are commonly found in all types of cooling systems, especially in low-flow areas.
- **Sulfate-reducing bacteria (SRB)** are the best known group of organisms involved in MIC. From the genera *Desulfovibrio*, *Desulfotomaculum*, and *Desulfomonas*, these anaerobic organisms (i.e., they live without directly metabolizing oxygen) metabolize sulfur in one form or another. The most widely known, *Desulfovibrio*, is often found in cooling systems, especially where oil or sludge is present.
- **Acid-producing bacteria (APB)** include the slime-forming bacteria *Pseudomonas*, *Aerobacter*, and *Bacillus*, which exude compounds such as formic, acetic, and oxalic acids in their metabolic processes. These organic acids cause low-pH conditions at local sites, resulting in corrosion. *Thiobacillus* is a common APB that oxidizes sulfur compounds, forming sulfuric acid, which is extremely corrosive and leads to localized underdeposit and pitting corrosion, often resulting in pinholes in pipework.
- **Biological deposits (BD)** such as algae, yeast, molds, fungi, and bacterial slimes can also cause MIC. Even in the absence of specific corrosive organisms, biological deposits provide the environment for corrosion through establishment of concentration cells, resulting in underdeposit corrosion. Biological deposits in general act as traps and food for other organisms, resulting in rapid growth. This complex matrix sets up a corrosion potential between adjacent areas of a metal surface that may have a different type of deposit.

To control and/or prevent MIC, it is important to understand the processes that cause it. An effective control and prevention program must address all types of biological growths in recirculating water systems.

Factors Affecting Corrosion

All cooling-water system metals of construction will corrode at some rate. Therefore, the rate of corrosion is of prime importance. This rate is commonly expressed in terms of penetration (thickness of metal lost) as millimetres per year (mm/yr). Table 2 provides guidelines for categorizing corrosion rates.

The following paragraphs describe the effects of various factors on corrosion.

Moisture. Corrosion does not occur in dry environments. However, some moisture is present as water vapor in most environments. In pure oxygen, almost no iron corrosion occurs at relative humidities up to 99%. However, when contaminants such as sulfur dioxide or solid particles of charcoal are present, corrosion can proceed at relative humidities of 50% or more. The corrosion reaction proceeds on surfaces of exposed metals such as iron and unalloyed steel as long as the metal remains wet. Many alloys develop protective corrosion-product films or oxide coatings and are thus unaffected by moisture.

Oxygen. Because oxygen is the primary consumer of electrons in cathode (rate-determining) reactions, the more oxygen, the greater the rate of corrosion. Within electrolytes, water solutions consisting of salts or acids, the presence of dissolved oxygen fuels the corrosion of ferrous metals by depolarizing the cathodic areas through reaction of oxygen with hydrogen (hydrolysis) generated at the cathode. Corrosion inhibitors act to stabilize and repair defects in naturally occurring protective film. Many corrosion inhibitors require that oxygen be present to achieve inhibition. At the anode, the ionic form of the metal is released into the electrolyte, thereby depleting or corroding the metal surface. In many systems, such as steam boilers or high-pressure water heaters, most of the dissolved oxygen and other gases are removed from the water by heating the feedwater above 93°C (deaeration) to reduce the potential for corrosion. In evaporative-cooling-water systems, the abundant presence of dissolved gases, including oxygen, and their effects should be considered in the design.

Solutes/pH. The acidic or basic nature of a solution is defined as pH; a neutral solution has a pH of 7. Acidic solutions are below pH 7, and basic solutions are above pH 7. The pH of cooling water influences the potential of most metals to corrode. Corrosion tends to increase as pH levels decrease (become more acidic). However, different metals show different corrosion curves with respect to pH. Because more basic solutions are generally less corrosive to ferrous

systems, it is practical in many water systems to minimize corrosion by adding caustic or alkaline buffering agents to raise and stabilize the pH to 9 or higher.

Concentration Cells and Chlorides. Because a corrosion cell is dependent on the ability of the electrolyte (water) to conduct the flow of electrons (an electrical current), increasing the dissolved solids increases the conductivity of the electrolyte and thus increases corrosion. For the corrosion reaction to proceed, a potential difference between anode and cathode areas is required. The potential difference between different locations on a metal surface is caused by differences in solute concentration in the localized environment. The enhancement of corrosion caused by such conditions is called **concentration cell corrosion**. These cells can be metal ions or oxygen concentration cells. Crevices, cracks, pits, and foreign deposits on the metal surface can create conditions that contribute to corrosion. The anodic area, where corrosion proceeds, is in the crevice or pit, or under the deposit. Whether the process is metal ion or oxygen concentration, available chlorides will accelerate the reactions. The process turns into an autocatalytic reaction, resulting in rapid destruction of the metal alloy. Though slow to start, once chlorides are introduced, this series of events leads to rapid failure of the metal unless the process is mechanically repaired or properly inhibited.

Galvanic (Dissimilar Metal) Corrosion. Another factor accelerates corrosion is the difference in potential of dissimilar metals coupled together and immersed in an electrolyte. The following factors control the severity of corrosion resulting from such dissimilar metal coupling:

- **Relative differences in position (potential) in the galvanic series,** with reference to a standard electrode (see [Figure 2](#)): the greater the difference, the greater the driving force of the reaction.
- **Relative area or mass relationship between anode and cathode areas:** because the amount of current flow and, therefore, total metal loss is determined by the potential difference and resistance of the circuits, a small anodic area corrodes more rapidly in the presence of a large cathodic area or mass. A larger anodic area or mass relative to the cathode reduces the penetration rate.
- **Polarization of either the cathodic or anodic area:** polarization can reduce the potential difference and thus reduce the rate of attack of the anode.
- **Ionic content of water or electrolyte:** as the concentration of the ionic components of the electrolyte increases, the resulting higher electrical conductivity increases the rate of galvanic corrosion.

Stress. Stresses in metallic structures rarely have significant effects on the uniform corrosion resistance of metals and alloys. Stresses in specific metals and alloys can cause corrosion cracking when the metals are exposed to specific corrosive environments. The cracking can have catastrophic effects on the usefulness of the metal. Almost all metals and alloys exhibit susceptibility to stress corrosion cracking in at least one environment. Common examples are steels in hot caustic solutions, high-zinc-content brasses in ammonia, and stainless steels in hot chlorides. Metal manufacturers have technical details on specific materials and their resistance to stress corrosion.

Temperature. Higher temperatures speed up chemical reactions. Thus, corrosion rates are greatest in areas such as heat exchangers where temperatures are the hottest. Even temperature variations within a single piece of metal will cause the warmer areas to become anodic to the cooler areas and corrode. According to studies of chemical reaction rates, corrosion rates double for every 10 K rise in temperature. However, such a ratio is not necessarily valid for nonlaboratory corrosion reactions.

An increase in temperature may increase the corrosion rate, but only to a point. Oxygen solubility decreases as temperature

increases and, in an open system, may approach zero as water boils. Beyond a critical temperature level, the corrosion rate may decrease because of a decrease in oxygen solubility. However, in a closed system, where oxygen cannot escape, the corrosion rate may continue to increase with an increase in temperature until the oxygen is used up. For those alloys, such as stainless steel, that depend on oxygen in the environment for maintaining a protective oxide film, the reduction in oxygen content caused by an increase in temperature can accelerate the corrosion rate by preventing oxide film formation.

Temperature can affect corrosion potential by causing a salt dissolved in the environment to precipitate on the metal surface as a protective layer of scale. One example is calcium carbonate scale in hard waters. Temperature can also affect the nature of the corrosion product, which may be relatively stable and protective in certain temperature ranges and unstable and nonprotective in others. An example of this is zinc in distilled water; the corrosion product is nonprotective from 60 to 87.8°C but reasonably protective at other temperatures.

Pressure. Where dissolved gases such as oxygen and carbon dioxide affect the corrosion rate, pressure on the system may increase their solubility and thus increase corrosion. Similarly, a vacuum on the system reduces the solubility of the dissolved gas, thus reducing corrosion. In a heated system, pressure may rise with temperature. It is difficult and impractical to control system corrosion by pressure control alone.

Flow Velocity. The effect of flow velocity on the corrosion rate depends on several factors, including

- Amount of oxygen in the water
- Suspended solids in the water
- Type of metal exposed (copper and iron both susceptible)
- Flow rate

In metal systems where corrosion products retard corrosion by acting as a physical barrier, high flow velocities may remove those protective barriers and increase the potential for corrosion. A turbulent environment may cause uneven attack, from both erosion and corrosion. This corrosion is called **erosion corrosion**. It is commonly found in piping with sharp bends where the flow velocity is high. Copper and softer metals are more susceptible to this type of attack. When flow velocity is low (less than 1 m/s), suspended solids can drop out and cause deposition as well as underdeposit corrosion, including concentration cell corrosion and microbial corrosion. Low flow velocity can also affect transport of corrosion inhibitors and polarization of corrosion cells.

Solids Management. The presence of solids, either suspended or deposited, in the waters of HVAC and process systems can cause abrasion, enhance corrosion, and reduce heat transfer. Suspended solids in flowing waters enhance erosion corrosion. Underdeposit corrosion can form under mats of dust, dirt, rust, silt, and other solids introduced into evaporative-cooling-water systems; mud, rust, and silts can deposit in closed-loop piping systems, especially in dead legs, storage and heat exchanger tanks, end bells, or cast iron boiler sections. See the section on Deposition, Scale, and Suspended-Solids Control for further discussion of control.

Other major factors affecting corrosion include those that have been discussed in the microbiological and fouling control programs. They center on the contaminants and/or conditions that work to

- Prevent inhibitors from reaching the metal surface
- Remove inhibitors and/or the protective films from the metal surface
- Promote the formation of biofilm and/or deposits under which corrosion can occur

Such conditions are common in systems with high suspended matter and/or poor microbiological control programs, as well as those systems with process contamination and/or poor deposit

control programs, including poor corrosion control programs contributing corrosion debris (by-products) as deposits.

Corrosion Preventive and Protective Measures

Materials Selection. Any piece of heating or air-conditioning equipment can be made of metals that are virtually corrosionproof under normal and typical operating conditions. However, economics usually dictate common material choices. When selecting construction materials, the following factors should be considered:

- Corrosion resistance of the metal in the operating environment.
- Corrosion products that may be formed and their effects on equipment operation.
- Ease of construction using a particular material.
- Design and fabrication limitations on corrosion potential.
- Economics of construction, operation, and maintenance during the projected life of the equipment (i.e., expenses may be minimized in the long run by paying more for a corrosion-resistant material and avoiding regular maintenance).
- Use of dissimilar metals should be avoided. Where dissimilar materials must be used, insulating gaskets and/or organic coatings must be used to prevent galvanic corrosion.
- Compatibility of chemical additives with materials in the system.

Protective Coatings. The operating environment has a significant role in the selection of protective coatings. The suitability of a coating for a particular environment also largely depends on the surface preparation of the metal to be protected, the coating thickness, and the coating application technique. The durability of the coating relies on the adhesion characteristics between the coating and the metal. Adhesion is largely the result of the surface preparation, including cleaning, degreasing, and the application of primers.

Defects in a coating are difficult to prevent. These defects can be either flaws introduced into the coating during application or mechanical damage sustained after application. To maintain corrosion protection, defects must be repaired both in the fabrication process and in the operational environment. Defects in coatings, called **holidays**, can lead to significant localized corrosion of the base metal, most commonly in the form of cathodic disbondment or oxide lifting. **Oxide lifting** occurs when anodic corrosion products accumulate under a coating adjacent to holidays, lifting the coating from the protected surface. **Cathodic disbondment** is the result of the cathodic reduction of dissolved oxygen, which, along with water, migrates under the coating from holidays. Once under the coating, blistering occurs, separating the coating from the protected surface.

Cycles of Concentration. Some corrosion control may be achieved by optimizing the cycles of concentration (the degree to which soluble mineral solids in the makeup water have increased in the circulating water because of evaporation). Generally, adjustment of the blowdown rate and pH to produce a slightly scale-forming condition (see the section on Scale and Deposit Formation Control) will result in an optimum condition between excess corrosion and excess scale.

Chemical Methods. Historically, several chemicals have been used to inhibit the corrosion process. It is important that the inhibitor not interfere with the heat transfer or other function of the metal. In general, corrosion inhibitors function in one of three ways:

- **Passivation:** these inhibitors act to form a thin protective oxide film on the metal surface. Nitrites and molybdates work in this way.
- **Precipitation:** these inhibitors contain materials that are precipitated out of solution to form protective films at sites in a corrosion cell. Zinc and phosphates work this way.

- **Adsorption:** these inhibitors are directly adsorbed onto the metal surface, where they form a protective layer. Organics usually function in this manner.

Many inhibitors work best when initially applied at two to three times their normal dosage for several weeks. This **pretreatment procedure** improves corrosion control by (more) rapidly establishing the protective inhibitor films to new metal surfaces. This procedure should also be repeated for start-ups that follow shutdowns and any time pH or other excursions occur.

Film-forming chemical inhibitors reduce or stop corrosion by interfering with the corrosion mechanism. Inhibitors usually affect either the anode or the cathode. The most common inhibitors today are molybdates, phosphates, zinc, phosphonates, silicates, nitrite-borates, aromatic azoles, and organics. Although very effective, chromate inhibitors are no longer used because of their environmental toxicity and the federal laws that have banned their use. The most important factor in an effective corrosion inhibition program is consistent control of both the corrosion inhibition chemicals and the key water characteristics. No program will be effective without controlling these factors.

Anodic corrosion inhibitors establish a protective film at the anode. They stop the corrosion cell by blocking the electrochemical reaction at the anodic site. Though these inhibitors can be very effective, they can also be very dangerous if insufficient anodic inhibitor is present, because the entire corrosion potential occurs at the unprotected anode sites. Severe localized pitting attack can occur at unprotected anodic sites if insufficient inhibitor is present.

Cathodic corrosion inhibitors establish a protective film at the cathode. They stop the corrosion cell by blocking the electrochemical reaction at the cathode. These inhibitors reduce the corrosion rate in direct proportion to the reduction of the cathodic area.

General corrosion inhibitors protect by forming a film on all metal surfaces, whether anodic or cathodic.

Cathodic Protection. Sacrificial anodes reduce galvanic attack by providing a metal (such as zinc or magnesium) that is lower on the galvanic series than either of the two metals that are coupled together. The sacrificial anode thereby becomes anodic to both metals and supplies electrons to these cathodic surfaces. Proper design and placement of these anodes are important. When properly used, they can reduce loss of steel from the tube sheet of exchangers using copper tubes. Sacrificial anodes have helped supplement chemical programs in many cooling-water and process water systems.

Impressed-current protection is a similar corrosion control technique that reverses the corrosion cell's normal current flow by impressing a stronger current of opposite polarity. Direct current is applied to an anode [inert (platinum, graphite) or expendable (aluminum, cast iron)], reversing the galvanic flow and converting the steel from a corroding anode to a protective cathode. The method is very effective in protecting essential equipment such as elevated water storage tanks, steel tanks, or buried pipelines and structures.

Corrosion Process Measurement

Uniform, or general, corrosion can be quantitatively measured. Localized corrosion, by definition, may only be observed in some cases, and is unobservable in most cases. Although the process of localized corrosion itself is not measurable, the damage to metals by localized corrosion attack can be assessed through various means, such as eddy current testing of chiller tubes.

Corrosion Coupons. The use of corrosion coupons is an accepted method for gaging quantitative analysis of uniform corrosion rates in both closed- and open-loop systems. Coupon specimens can sometimes exhibit results of localized attack, most frequently from underdeposit and/or microbially influenced corrosion. Evidence of excessive localized attack on a coupon specimen may invalidate the

coupon specimen from further inclusion in a test or series evaluation. Careful selection, handling, placement, alignment, and recording of coupon specimens is required for accurate corrosion coupon test results. Flow rates and velocities of the fluid through the coupon rack are essential to accurate results. Fluid velocity of 1 m/s is normally used, and velocities in excess of 1.5 m/s may cause erosion, particularly of soft metals such as copper. Ideally, constant flow should be maintained throughout the test period. Coupon specimens should not be disturbed during a test.

Commonly used coupon specimens are mild steel and copper. Less-frequently used are coupons of admiralty grades of brass, and various grades of stainless steel. Placement of the least noble coupon specimen should precede progressively more noble coupons within the rack in the direction of fluid flow.

Because of high initial corrosion rates of the specimen coupon metals, long-duration tests of coupons (60, 90 days) yield more-accurate results in operating systems than shorter tests (15, 30 days). For comparison and trend analysis, a series of tests should be conducted using the same or similar exposure lengths.

Electronic corrosion sensors or probes can be used to determine uniform corrosion rates in a system or to augment a corrosion coupon program. Many different types of probes and systems are available, including electric resistance and inductive resistance probes. Linear polarization resistance probes give real-time feedback of corrosion rates. However, because rates of uniform corrosion are rarely consistent over time, the readings from linear polarization devices should be monitored or logged to assess trends in the corrosion rates and system stability. Electronic sensors will not exhibit the clear differences between uniform and localized attack that may be observable on coupon specimens. Consult a water treatment professional about the proper type of probe for the specific application and water treatment program.

White Rust on Galvanized Steel Cooling Towers

White rust is a zinc corrosion product that forms on galvanized surfaces. It appears as a white, waxy, or fluffy deposit composed of loosely adhering crystalline form of zinc carbonate hydroxide. There is some debate in the literature as to the specific chemical composition of white rust and that of the desirable passivated, durable zinc surface, though they are deemed to be very similar in composition, if not identical. For the purposes of this chapter, and to clearly differentiate the two, white rust is referred to as zinc carbonate hydroxide and the desired passivated surface as zinc carbonate.

The most damaging white rust forms on submerged and consistently wetted galvanized surfaces. This loose crystal structure of zinc carbonate hydroxide allows continued access of the electrolytic fluid (water) to quickly expose successive layers of the zinc coating over carbon steel sheet or plate, in effect accelerating the zinc anodic reaction locally. This unusually rapid reduction of zinc allows corrosion of the exposed carbon steel, which can affect the life cycle of galvanized steel cooling towers under certain conditions. These conditions are generally accepted to be found in waters with pH below 6 or above ~8.5, and with carbonate (P-alkalinity > 0) and hydroxide alkalinity species present in the solution. Further acceleration of white rust formation can be caused by calcium hardness below 50 ppm (as CaCO₃), requiring the evaluation of the use of water softeners on makeup water during passivation.

Today's cooling tower treatment programs generally involve the addition of phosphate-polymer-based scale and corrosion inhibitors and operating cooling-water systems at alkaline pH. Water chemistry at these higher pH levels (>8 to 9+) is naturally less corrosive to steel and copper, but can create an environment where white rust on galvanized steel can occur. Also, some scale prevention programs soften the water to reduce hardness, rather than use acid to reduce alkalinity. Resulting soft waters with <50 ppm hardness (as CaCO₃) can also be corrosive to galvanized steel.

White Rust Prevention. White rust can be prevented in new galvanized cooling towers by promoting the formation of a nonporous surface layer of basic zinc carbonate. This barrier layer is formed during a process called **passivation** and normally protects the galvanized steel for many years. Passivation is best accomplished by controlling pH during initial operation of the cooling tower. Controlling the cooling-water pH in the range of 7 to 8 for 45 to 60 days usually allows passivation of galvanized surfaces to occur. Excursions of cooling-water pH (<7 and >8) during passivation is undesirable, and consistent monitoring and control are essential to prevent white rust formation. In addition to pH control, initial operation during passivation with moderate hardness levels of 100 to 300 ppm as CaCO₃ and alkalinity levels of 100 to 300 ppm as CaCO₃ will promote passivation. Where pH control is not possible or practical (e.g., makeup water is >8), phosphate-based inhibitors may help protect galvanized steel. Application of an inhibitor in lieu of initial passivation by pH control may later expose the galvanized surfaces to white rust formation should the inhibitor fall below recommended residuals and the pH exceed 8. A water treatment company should be consulted for specific formulations.

5. BIOLOGICAL GROWTH CONTROL

Cooling-water systems provide almost ideal conditions for the growth and proliferation of microorganisms: abundant water, good aeration, and a continuous supply of nutrients. The nutrients may include inorganic and organic compounds added directly to the systems (to fight corrosion/scale/foam) or introduced via the air that is constantly being washed and scrubbed by a cooling tower or air washer. Another major source of nutrient supply is leakage or process contamination associated with plant manufacturing processes being served by the cooling-water system.

Problems associated with the uncontrolled growth of microorganisms in cooling-water systems can be categorized in the following four areas:

- Plugging and fouling by biological slime (biofilm/biomass)
- Biodeterioration (e.g., wood rot)
- Microbiologically influenced/induced corrosion (MIC)
- Potential health/safety issues (e.g., disease-causing bacteria)

More cooling-water treatment programs fail because of lack of microbiological control than from any other treatment problem. Scale, corrosion, and fouling are often just symptoms of poor microbiological control. Makeup water and wind can carry microorganisms into a cooling-water system. Uncontrolled microbiological fouling can lead to problems throughout the cooling-water system. Corrosion occurs under the bacterial slime layer. Inorganic foulants are trapped in this slime layer, compounding problems. The effects of uncontrolled microbiological activity and fouling may negate the effectiveness of even the best programs for scale prevention and corrosion inhibition. Appropriate biocides must be selected to handle the most prevalent problems first, perhaps in conjunction with dispersants to penetrate and remove deposits. Effective microbiological control is an absolute necessity for a cooling-water program to be successful.

An effective microbiocide program to control the growth of microorganisms involves four steps:

1. Identify the types and concentrations of microorganisms present in the cooling system.
2. Select proper biocides based on system design, discharge restrictions, and types of microorganisms.
3. Implement proper application, dosage, and control of the selected biocides.
4. Maintain seasonal disinfection cleanings.

Microorganisms found in cooling-water systems generally fall into one of three categories: (1) algae, (2) bacteria, or (3) fungi. These organisms can enter a cooling system in a variety of ways: through the makeup water supply; from the atmosphere during normal operation; or from accumulations of environmental organic matter, such as insects, bird droppings, grass clippings, and construction debris. Microbial growth can interfere with a cooling operation by causing fouling or corrosion, and may pose a health hazard. Heating equipment operates above normal biological temperature limits and therefore has fewer microbial problems.

When considering biological growth in a cooling system, it is important to distinguish between planktonic (free-living) and sessile (attached) microorganisms:

- **Planktonic bacteria** are suspended in the water and sometimes referred to as “free floaters” or “swimmers.” They are aerobic bacteria that thrive in an oxygenated environment. They are not harmful to the cooling system, because they do not cause deposits or corrosion, but they can provide nutrients for other microorganisms. In addition, some planktonic bacteria, such as *Legionella pneumophila*, are pathogenic and can present a significant human health risk.
- **Sessile bacteria** are nonswimming (attached) bacteria, sometimes called “stickers.” Sessile organisms cause the majority of the problems in cooling-water systems, because they are not detected in total bacteria counts and tend to be overlooked until problems arise. They establish themselves by attaching to contact surfaces to develop microcolonies with dense biomatrix structures. Sessile bacteria types include slime-formers and anaerobic (corrosive) bacteria. Slime-formers can grow and form gelatinous deposits on almost any surface in contact with the cooling water. These deposits can grow so large that they restrict water flow and interfere with heat transfer; they also may promote underdeposit corrosion. Usually, if slime-formers are present in the system, deposits can be felt on the sides of the cooling tower basin just below the water level. Anaerobic bacteria thrive in oxygen-deprived environments and often establish colonies beneath slime deposits or under other types of deposits. Surface microbial measurements using special coupons and/or other monitoring devices can be used to monitor sessile bacteria.

Biological fouling can be caused by a wide variety of organisms that produce biofilm and slime masses. Slimes can be formed by bacteria, algae, yeasts, or molds and frequently consist of a mixture of these organisms combined with organic and inorganic debris. Among the problematic bacterial species, sulfate-reducing bacteria (SRB) and iron-related bacteria (IRB) are the most concerning species after *Legionella*. Their presence suggests a potential for severe corrosion and fouling. IRB are commonly found in tubercles and account for assimilation of ferrous ions to form mounds of ferric hydroxide, whereas SRB are usually found in the bottom of tubercles with black iron sulfides and sometimes elemental sulfur. The sulfur products give off a rotten-egg smell. They signal the presence of acid-producing bacteria and deep penetrating pits.

Because biofilm microorganisms can dramatically enhance, accelerate, and, in some cases, initiate localized corrosion (pitting), they are tested and monitored for critical heat transfer operations. Monitoring methods include the following:

- Visual and tactile inspection
- Water analysis for ammonia, chemical oxygen demand (COD), total organic carbon (TOC), adenosine triphosphate (ATP), bacteria speciations, and planktonic plate counts
- Online biofilm monitors, including corrosion-resistant coupons, disks/plugs, electrochemical sensors, thermal gradient sensors, and sidestream devices to track hydrodynamic pressure differential and heat transfer

Microorganisms can influence localized corrosion directly by their metabolism or indirectly by the deposits they form. Indirect influence may not be mediated by simply killing the microorganisms; deposit removal through disinfection cleaning is usually necessary, whereas direct influence can be substantially mediated by inhibiting microorganism metabolism with proper choice of a biocide program.

Algae uses energy from the sun to convert bicarbonate or carbon dioxide into biomass. Algal mass can block piping, distribution holes, and nozzles.

Control Measures

Eliminating sunlight from wetted surfaces such as distribution troughs, cooling media, and sumps significantly reduces algae growth. A distribution deck cover, which drastically reduces the sunlight reaching the algae, is one of the most cost-effective control devices for a cooling tower.

Eliminating dead legs and low-flow areas in the piping and the cooling loop reduces biological growth in those areas. Careful selection of materials of construction can remove nutrient sources and environmental niches for growth and also helps mitigate corrosion. Maintaining a high-quality makeup water supply with low bacterial counts also reduces biological growth. Equipment should be designed with adequate access for inspection, sampling, and manual cleaning.

Effective biocide treatment is usually a combination of an oxidizing biocide with a nonoxidizing biocide. The oxidizer may be fed continuously or intermittently and alternately with a nonoxidizer. A biodispersant (surfactant) is often incorporated to enhance biocide performance. Mechanical aids include modification of surface texture, submicron filter media, fine strainers, scrapers/brushes, and flow and temperature control. Nonchemical treatment approaches include biocidal paint, ultraviolet light, sonication with ultrasound, and modification of contact surface material.

Sometimes, effective control of slime and algae requires a combination of mechanical and chemical treatments. For example, when a system already contains a considerable accumulation of slime, a preliminary mechanical cleaning makes the subsequent application of a biocidal chemical more effective in killing the growth and more effective in preventing further growth. A build-up of scale deposits, corrosion product, and sediment in a cooling system also reduces the effectiveness of chemical biocides. Routine maintenance disinfection cleaning of cooling towers, including the use of high-level chlorination and a biodispersant, helps control *Legionella* bacteria as well as other microorganisms. Sidestream filtration and monitoring devices such as corrosion coupons, test spools, and biofilm sensors can enhance control of biofilm growth. Alternating two different types of biocide can overcome resistance developed by bacteria against a single biocide. The two different types should include two different kill mechanisms.

Microbiocides. Chemical biocides used to control biological growth in cooling systems fall into two broad categories: oxidizing and nonoxidizing biocides.

Oxidizing biocides. These substances [chlorine, bromine, ozone, iodine, chlorine dioxide, and halogen-releasing compounds such as bromochlorodimethylhydantoin (BCDMH or BCD)] are among the most effective biocide chemicals used in water treatment. However, they are not always effective or appropriate for use in cooling-water systems with high organic loading, high temperatures, and/or systems with corrosion or contaminant (compatibility) issues. In air washers, the odor may become offensive to building/facility occupants, or the exit air (to the building/facility) may be too corrosive for the environment. In wooden cooling towers, high levels of oxidizing biocides can cause delignification. Overdosing of oxidizing biocides may cause corrosion issues with metallic components in any system. The accurate feed and control of oxidizing biocides for the most

effective, efficient, and safe application requires using appropriate feed and control equipment. In many systems, the most effective use of oxidizing biocides is to maintain a constant low-level residual in the system. However, if halogen-based oxidizing biocides are fed intermittently (slug dosed), a pH below 8 is most advantageous, because of the pH-dependent dissociation curve where the halogen (particularly chlorine) is more prevalent in the more biocidally active (hypohalous acid) form. The residual oxidizing biocide concentration should be tested on a routine basis. Most halogenation programs can benefit from the use of dispersants or surfactants (chlorine helpers) to penetrate and break up microbial masses and biofilm.

Chlorine has been the oxidizing biocide of choice for many years, either as chlorine gas or in liquid form as sodium hypochlorite. Other forms of chlorine, such as powders or pellets or calcium hypochlorite sticks, and chlorine-releasing compounds (e.g., chloramines, chloroisocyanurates) are also available. It can also be produced electrolytically with brine on site. Use of chlorine gas is declining because of health and safety concerns involved in handling this material and because of environmental pressures concerning the formation of EPA-regulated halogenated disinfection by-products. In potable hot-water systems, chlorine loses efficacy up to 70% at temperature of 60 to 71°C.

Bromine is usually produced through reactions of an oxidizer such as sodium hypochlorite with sodium bromide on site, or by release from solids of chlorobromohydrantoin compounds. Bromine has certain advantages over chlorine: it is less volatile, and bromamines break down more rapidly than chloramines in the environment. Also, when slug feeding biocide in high-pH systems, hypobromite ions may have an advantage because their biocidal power is better than that of hypochlorite ions. This effect is less important when biocides are fed continuously at low dosage. Like chlorine, bromine can affect the environment with formation of EPA-regulated halogenated disinfection by-products.

Ozone is an allotropic form of oxygen consisting of three oxygen atoms (O₃) that exists as a gas. As a biocide, it has several advantages compared to chlorine: it does not produce halogenated disinfection by-products, it breaks down to nontoxic compounds rapidly in the environment, it is more potent than chlorine in destructing biofilms, and it requires significantly less chemical handling. The disadvantages of ozone are its short half-life, instability for storage, and reaction by-products that are more biodegradable than their precursors. Use of ozone-generating equipment in an enclosed space requires safety protocols to protect operators from the toxic gas.

Water conditions should be reviewed to determine the need for scale and corrosion inhibitors and then, as with all oxidizing biocides, inhibitor chemicals should be carefully selected to ensure compatibility. To maximize the biocidal performance of ozone, the injection equipment should be designed to provide adequate contact of the ozone with the circulating water. In larger systems, care should be taken to ensure that the ozone is not depleted before ozonated water has circulated through the entire system.

Iodine is provided in pelletized form, often from a rechargeable cartridge. Iodine is a relatively expensive chemical for use on cooling towers and is probably only suitable for use on smaller systems.

Chlorine dioxide, a gas, is effective in low concentrations, 0.2 to 0.5 ppm residual. It must be generated on site. Unlike ozone, it is not affected by pH, and has a longer half-life and higher penetrating power because of lower oxidizing potential. It is usually generated with sodium chlorite precursor by either an electrolytic generator or reactions with acids. Its drawbacks are instability in storage, costly generating equipment, and precursors and acid salt in the end product solution.

Hydrogen peroxide (H₂O₂) is a liquid that is usually available in concentrations of 50% or less, by mass, in water. Hydrogen peroxide is considered one of the most environmentally friendly oxidizing biocides, because it degrades to water; however,

concentrated hydrogen peroxide will react in a violent manner when it comes into contact with organic chemicals and materials.

Nonoxidizing Biocides. Nonoxidizing biocides destroy organisms either by poisoning the organism, blocking its ability to uptake energy, or disrupting its protective coating (cellular membranes) and exposing the organism to a hostile environment. Most nonoxidizers are also known as **biostats**, which means they inhibit growth of microorganisms. Examples include quaternary ammonium compounds, organosulfur compounds, and aldehyde release treatments.

When selecting a nonoxidizing microbiocide, many factors must be considered for its effective and efficient use. Such considerations include system pH and relevant water chemistry, chemical compatibility with other treatment products and system contaminants, as well as the system turnover rate or holding time index (HTI) for adequate microbial contact time. The following is a list of nonoxidizing biocides common to the industry:

- Quaternary ammonium compounds
- Polyquats
- Methylene bis(thiocyanate) (MBT)
- Isothiazolones
- Tetrahydro-3,5-dimethyl-2H-1,3,5-thiadiazine-2-thione (Thione)
- Tributyl tetradecyl phosphonium chloride (TTPC)
- Bis(tributyltin) oxide (TBTO)
- Carbamates/Dithiocarbamates
- 2-(Decylthio)ethanamine (DTEA)
- Glutaraldehyde
- Dodecylguanidine (Guanides)
- Tetrakis(hydroxymethyl)phosphonium sulfate (THPS, TKHPS)
- 2-(tert-butylamino)-4-chloro-6-(ethylamino)-s-triazine (TBZ, Tertbutylazine)
- 2-2-Dibromo-3-nitropropionamide (DBNPA)
- 2-Bromo-4-hydroxyacetophenone (BHAP)
- 2-Bromo-2-nitropropane-1,3-diol (Bronopol)
- Bromo-nitrostyrene (BNS)
- Proprietary blends

The manner in which nonoxidizing biocides are fed is important. Sometimes, the continuous feeding of low dosages is neither effective nor economical. Slug feeding large concentrations to achieve a toxic level of the chemical in the water for a sufficient time to kill the organisms present can show better results. Water blowdown rate and biocide hydrolysis (chemical degradation) rate affect the required dosage. The hydrolysis rate of the biocide is affected by the type of biocide, along with the temperature and pH of the system water. Dosage rates are proportional to system volume; dosage concentrations should be sufficient to ensure that the contact time of the biocide is long enough to obtain a high kill rate of microorganisms before the minimum inhibitory concentration of the biocide is reached. The period between nonoxidizing biocide additions should be based on the system half-life, with sequential additions timed to prevent regrowth of bacteria in the water. When two nonoxidizing biocides are used, it is important to select the two biocides based on two different kill modes of action to overcome resistance developed by microbes.

Handling Microbiocides. All microbiocides must be handled with care to ensure personal safety. In the United States, cooling-water microbiocides are approved and regulated through the EPA and, by law, must be handled in accordance with labeled instructions. Maintenance staff handling the biocides must read the material safety data sheets (MSDS) and be provided with all the appropriate safety equipment to handle the substance. An automatic feed system is preferred, to minimize and eliminate handling of biocides by maintenance personnel.

Other Biocides. **Ultraviolet (UV) irradiation** deactivates microorganisms as the water passes through a quartz tube. The intensity of the light and thorough contact with the water are critical

in obtaining a satisfactory kill of microorganisms. Suspended solids in the water or deposits on the quartz tube significantly reduce the effectiveness of this treatment method. Therefore, a filter is often installed upstream of the UV lamp to minimize these problems. Because ordinary (low-energy) ultraviolet light leaves no residual material in the water, sessile organisms and organisms that do not pass the light source are not affected by the ultraviolet treatment. Ultraviolet irradiation may be effective on humidifiers and air washers where the application of biocidal chemicals is unacceptable and where 100% of the recirculating water passes the lamp. Ultraviolet irradiation is less effective where all the microorganisms cannot be exposed to the treatment, such as in cooling towers. Ultraviolet lamps require replacement after approximately every 9000 h of operation.

Metallic ions, namely copper (Cu) and silver (Ag), can effectively control microbial populations in municipal water systems when the ionization systems that produce them are properly maintained, operated, and appropriately applied. Either singularly or in combination, copper and silver ions are released into the water via electrochemical means to generate 0.4 to 0.8 mg/L of copper and 40 to 80 µg/L of silver. The ions assist in the control of bacterial populations. Copper, in particular, effectively controls algae.

Legionella and Legionnaires' Disease

Legionellosis is any disease caused by *Legionella* bacteria. **Legionnaires' disease**, a form of legionellosis, is a potentially fatal, pneumonia-like illness primarily caused by *Legionella pneumophila*, one of the more than fifty known species of *Legionella*.

Legionella are common warm-water microorganisms that are mostly found in surface waters (lakes, ponds, rivers, streams) but can also be found in groundwater sources, including some soils. *Legionella* tend to grow in biofilm or slime on the surfaces of lakes, rivers, and streams. They can easily adapt to conditions within water distribution systems, thereby escaping municipal water plant disinfection (chlorination) treatment in some instances, and show up in municipal water supplies. They can, therefore, be found in domestic (potable) water plumbing and associated building water systems such as cooling towers, spas, water fountains, and other water-use systems. Within these systems, *Legionella* can find favorable conditions for growth and amplification, and pose the risk for human disease.

The mere presence of *Legionella* does not, in and of itself, result in disease. Several conditions and factors must occur for *Legionella* to cause disease. Primarily, there must be a sufficient quantity and/or virulent form of the bacteria made transmittable and then transmitted to a susceptible host. Transmission occurs when a host inhales tiny water droplets (mists or vapor aerosols) containing *Legionella* from a water-aerosolizing device and/or there is aspiration of the same. Aspiration of water can also occur during the normal drinking and swallowing process consequent to the response of a choking or gag reflex. Inhalation and aspiration provide the entry of infectious *Legionella* to the deep, distal parts (alveoli) of the lungs where they take over and promote the pneumonia of Legionnaires' disease. The dose of *Legionella pneumophila* (or other species of *Legionella*) required to infect humans is not known. It is most probably influenced by host susceptibility.

Legionella grow well and amplify in warm-water environments and systems that provide favorable conditions for bacterial growth and the formation of biofilm. The optimum temperature range for growth is 32.2 to 40.6°C. The subsequent use or release of water from such systems harboring *Legionella*, through faucets, shower sprays, humidifying, aerosolizing (misting) devices, or other operational spray or drift mechanisms of the system, may transmit the potential disease-causing bacteria to susceptible hosts.

Legionella pneumophila was first identified in 1977, following an outbreak of disease associated with a Philadelphia host hotel for

an American Legion convention in 1976. Since then, national surveillance systems and research studies have been established around the world. In recent years, with improved capabilities and changes in clinical methods of diagnosis, there has been an upsurge in reported cases in many countries. Environmental studies continue to provide information and identify novel sources of infection, leading to regular revisions of guidelines and regulations. As of 2014, an estimated 8000 to 18 000 people are hospitalized with Legionnaires' disease each year in the United States, according to the Centers for Disease Control and Prevention (CDC), and the disease has a 5 to 30% mortality rate (www.cdc.gov/legionella/about/).

Outbreaks of Legionnaires' disease receive media attention. However, this disease more often occurs as single, isolated cases not associated with any recognized outbreak. When outbreaks do occur, they are usually in the summer and early autumn, though cases may occur at any time of year.

Water treatment microbial control programs should also include a risk assessment for *Legionella* control and disease prevention. This includes the effectiveness of treatment products and the program to control *Legionella* and the conditions favorable for its growth and amplification, including the accumulation of biofilm (slime/biomass), the presence of amoebae and other protozoans that harbor it, as well as the potential of the water system to produce aerosols and provide routes of aerosol transmission to susceptible human populations.

See ASHRAE *Guideline 12-2000* for further information.

6. COOLING TOWER SYSTEMS START-UP AND SHUTDOWN

The following guidelines are for start-up (or recommissioning) and shutdown of cooling tower systems.

Start-Up and Recommissioning for Drained Systems

1. Inspect tower interior for airborne debris and storm or weather-related damages, and determine the extent of cleaning and repairs needed.
2. Clean all debris, such as leaves and dirt, from the cooling tower.
3. Close building air intakes in the area of the cooling tower to prevent entrainment of biocide and biological aerosols in the building's air-handling system.
4. Fill the system with water. While operating the condensing water pump(s) and *before operating the cooling tower fans*, execute one of the following two biocidal pretreatment programs:
 - a. Resume treatment with the biocide that had been used before shutdown. Use the services of the water treatment supplier. Maintain the maximum recommended biocide residual for the specific biocide for a period sufficient to bring the system under good biological control (residual and time varies with the biocide).
 - b. Treat the system with sodium hypochlorite at a level of 4 to 5 mg/kg free chlorine residual at a pH of 7.0 to 7.6. The residual level of free chlorine should be held at 4 to 5 mg/kg for 6 h.
5. Once the biocidal pretreatment program has been successfully completed, turn on the fan and then put the system in service. The standard water treatment program (including biocide treatment) should be resumed at this time.

Start-Up and Recommissioning for Undrained (Stagnant) Systems

1. Inspect tower interior for airborne debris and storm or weather-related damages, and determine the extent of cleaning and repairs needed.
2. Remove accessible solid debris from bulk water storage vessel.

3. Close building air intakes in the area of the cooling tower to prevent entrainment of biocide and biological aerosols in the building's air-handling system.
4. Perform one of the two biocide pretreatment procedures (described in the section on Start-Up and Recommissioning for Drained Systems) directly to the bulk water storage vessel (cooling tower sump, draindown tank, etc.). *Do not circulate stagnant bulk cooling water over cooling tower fill or operate cooling tower fans during pretreatment.*
5. Stagnant cooling water may be circulated with condenser water pumps if tower fill is bypassed. Otherwise, add approved biocide directly to the bulk water source and mix with manual or side-stream flow methods. Take care to prevent creating aerosol spray from the stagnant cooling water from any point in the cooling-water system.
6. When the biocidal pretreatment is successfully completed, the cooling water should be circulated over the tower fill. Once the biocide treatment has been maintained at a satisfactory level for at least 6 h, the cooling tower fans may then be operated safely.

Shutdown: When the system is to be shut down for an extended period, the entire system (cooling tower, system piping, heat exchangers, etc.) should be flushed and drained using the following procedure:

1. Add a dispersant and biocide to the system and recirculate for 12 to 24 h. Confer with a water treatment consultant for suitable chemicals and dosage levels.
2. Shut down pumps and completely drain all water distribution piping and headers, as well as the cooling loop. Remove water and debris from dead heads and low areas in the piping, which may not have completely drained.
3. Rinse silt and debris from the sump. Pay special attention to corners and crevices. Add a mild solution of detergent and disinfectant to the sump and rinse. If the sump does not completely drain, pump out the remaining water and residue.
4. If the equipment cannot be completely drained and is exposed to cold temperatures, freeze protection may be required.
5. Significant protection can be afforded drained piping and systems with nitrogen blanketing or vapor-phase corrosion inhibitors.

7. HEATING AND STEAM-GENERATING SYSTEMS

Steam and hot-water systems can be classified into three broad groups: (1) steam and hot water for space heating and humidity control in commercial and residential HVAC systems and many industrial plants; (2) steam for industrial process heating and for use as a process reactant in chemical plants, paper mills, etc.; and (3) steam to drive turbines for electric power generation. The American Society of Mechanical Engineers (ASME) classifies boilers into three basic types: fire-tube, water-tube, and electric (ASME 2015). Boilers are also classified according to pressure, materials of construction, size, tube contents (i.e., water-side or fire-side), firing, heat source, or circulation. A general understanding of boiler design and classifications, as well as requirements of the system, is essential to ensure the system receives proper care to maintain reliability. One of the most important classifications of boiler systems is the end use of the steam or hot water. The focus of this chapter is on steam and hot-water boiler systems for space heating and humidity control in commercial and residential HVAC systems and some industrial plants.

Hot-water heating and low-pressure (103 kPa or less) steam systems with >95% condensate return are similar to closed-loop cooling systems, except with reversed heat-exchange processes. The hot water or steam adds heat to an HVAC system or to an industrial

process. The hot-water temperature is maintained either by heat exchange with a steam source or by direct firing in a hot-water-heating boiler.

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

Steam Boiler Systems

Scale in boilers is a direct result of precipitation of the calcium, magnesium, iron, and silica minerals present in the boiler feedwater. Scale can be prevented by removing a portion of the scale-forming ingredients prior to the boiler with external water-softening equipment, or within the boiler itself with internal boiler water treatment.

One of the most troublesome deposits frequently encountered in steam boilers is iron and combinations of iron with calcium and phosphate used in boiler water treatment. These sticky, adherent sludge deposits are caused by excessive amounts of iron entering the boiler with the feedwater. The iron is in the form of iron oxide or iron carbonate corrosion products. It is a result of corrosion products from the sections prior to the boiler, such as steam and condensate lines, condensate receivers, deaerators, and boiler feedwater lines. A program for preventing scale deposits must include treatment to prevent this troublesome type of sludge deposit.

Many treatment methods are available for steam-producing boilers; the method selected depends on

- Makeup water quality
- Makeup water quantity (or percentage condensate return)
- Pretreatment equipment
- Boiler operating conditions
- Steam purity requirements
- Economics

When possible, the removal of scale-forming minerals and other objectionable minerals from the water before it enters the boiler system is preferred to internal boiler treatment. The internal boiler treatment program should be designed as a polishing tool to ensure clean heat transfer surfaces.

The selection of the proper pretreatment system depends on boiler type, size, source water mineral content, and the desired operator involvement in system operation. This section discusses typical pretreatment solutions for steam boilers in HVAC applications. Some of the pretreatment system components will have a positive effect on water and energy usage. Some components will also require additional regenerants as consumables. Selection criteria should include the effects of all components, as well as local water type and sanitary discharge regulations.

Boiler External Pretreatment Categories

Ion Exchange Resin. Ion exchange resin allows for specific ions or groups of ions to be removed from the water and be exchanged for another ion that will have negligible negative effect on the steam system. These resin beads then require regeneration to remove the objectionable ions to drain and replenish the reaction sites with the regenerant ions. The ion exchange resins can be classified in two groups: anion exchanger and cation exchanger.

Zeolite softeners are cation exchangers that remove calcium and magnesium (and some dissolved iron) from the water and replace them with sodium ions, effectively removing the scaling minerals from the makeup water. The resin is regenerated with sodium chloride salt (NaCl) solution. It is also possible to regenerate with potassium chloride salt (KCl) to minimize sodium effluent during regeneration. Water softeners have negligible effect on the total dissolved solids of the water.

Chloride cycle dealkalizers are anion exchangers that remove carbonates from the water and replace them with chloride ions. This minimizes carbonic acid formation in the condensate network, and reduces chemical consumption. Reducing the carbonate alkalinity of the incoming water may also offer opportunities to reduce boiler blowdown rates, resulting in water and energy savings. The resin is regenerated with sodium chloride salt (NaCl) solution and sodium hydroxide (caustic soda, NaOH). The chloride cycle dealkalizer must be installed downstream of a water softener.

Deionizers use both anion and cation resin. Ions are removed through a mixed-bed deionizer or individual anion and cation exchanger vessels used in series. This exchanger system removes virtually all anions and cations in the incoming water, replacing them with H^+ and OH^- , which in turn forms water. Mixed-bed deionizers are typically regenerated off site by a third-party service. Individual anion and cation exchangers are regenerated with acid and caustic soda, and require increased operator involvement. The water produced by a deionizer is extremely low in dissolved solids and offers significant reductions in boiler blowdown requirements, leading to water and energy savings. This water quality also minimizes carbonic acid formation in the condensate network, and reduces chemical consumption. Deionizers are typically seen in clean-steam applications.

Membrane Separation. Membrane separation allows water to pass through a semipermeable membrane while preventing certain or all dissolved mineral ions from passing through with the water. This is done by cross-flow filtration. The dissolved mineral ions are flushed to drain via a concentrate (reject) stream. Membrane separation increases water usage because of the increased water requirement of the concentrate stream. It may be possible to reuse this concentrate stream for other applications on site.

Reverse osmosis (RO) produces the highest-quality (lowest dissolved mineral content) of all membrane separation technologies. The water quality produced by RO systems is very low in dissolved solids and offers significant reductions in boiler blowdown requirements, leading to energy savings. This water quality also minimizes carbonic acid formation in the condensate network, and reduces chemical consumption. Reverse osmosis typically does not save water. The concentrate stream causes the total pretreatment system water input to increase by 20 to 50%.

Mechanical Deaeration/Deaerators. The purposes of deaeration are to (1) remove oxygen, carbon dioxide, and other noncondensable gases from boiler feedwater; and (2) heat the incoming makeup water and return condensate to an optimum temperature for minimizing solubility of the undesirable gases, providing the highest temperature water for injection to the boiler. A deaerator is a vessel specifically designed to preheat the feedwater and remove dissolved gases, primarily oxygen. Deaerators and feedwater heaters function on the principle that the dissolved gases are decreasingly soluble as the temperature of their solution is raised. However, even the most efficient deaerators cannot remove all of the dissolved oxygen. Although these deaerators can reduce dissolved oxygen to a $7 \mu\text{g/L}$ level, trace amounts are still present and can cause corrosion-related problems. Chemical oxygen scavengers then must be added to the feedwater, preferably in the storage section of the deaerator or feedwater tank, to remove the final traces of dissolved oxygen. The most commonly used oxygen scavenger is sodium sulfite. It is very effective and can be easily measured in the water.

In smaller boilers, mixing of makeup water and condensate normally occurs in an unpressurized vessel called a feedwater tank. Although much less sophisticated and efficient than a deaerator, a feedwater tank serves much the same purpose, which is to preheat the feedwater and promote removal of harmful dissolved gases. Whether a deaerator or a feedwater tank is used, its proper operation is important to the overall success of the water treatment program. Unless proper treatment measures are taken, dissolved gases can cause major corrosion damage in feedwater lines, economizers, boiler internals, steam-operated equipment, and condensate return piping.

Boiler Feedwater

After pretreatment to remove hardness and other problem impurities, the makeup water combines with returned condensate to become boiler feedwater. In larger boilers, the mixing of makeup water and condensate normally occurs in a deaerator. The most common sources of corrosion in boiler systems are dissolved gases: oxygen, carbon dioxide, and ammonia. Of these, oxygen is the most aggressive. Dissolved oxygen is undesirable because it can cause major corrosion damage in the boiler system and greatly increases treatment chemical requirements. The importance of eliminating oxygen as a source of pitting and iron deposition cannot be overemphasized. Even small concentrations of this gas can cause serious corrosion problems.

Makeup water introduces appreciable amounts of oxygen into the system. Oxygen can also enter the feedwater system from the condensate return system. Possible return line sources are direct air leakage on the suction side of pumps, systems under vacuum, the breathing action of closed condensate receiving tanks, open condensate receiving tanks, and leakage of non-deaerated water used for condensate pump seal and/or quench water. With all of these sources, good housekeeping is an essential part of the preventive program.

Boiler Internal Treatments

Even after the best and most appropriate external treatment of the water source, boiler feedwater (including return condensate) still contains impurities that could adversely affect boiler operation. Internal boiler water treatment is then applied to minimize the potential problems and to avoid catastrophic failure, regardless of external treatment malfunction.

Prevention of Scale. After the feedwater is pretreated, scale is controlled with phosphates, acrylates, polymers, chelates, and coagulation programs. Chelates, polymers, and acrylates work by binding the hardness, thereby preventing precipitation and scale formation. Phosphates and coagulation programs work in combination with sludge conditioners (tannins, lignins, starches, and synthetic polymers) to produce a softened precipitate that is removed by blowdown of the boiler.

Prevention of Corrosion and Oxygen Pitting. Although boilers can corrode as the result of low boiler water pH or misuse of certain chemicals, corrosion is primarily caused by oxygen. After mechanical deaeration, boiler feedwater must be treated chemically to remove the final traces of dissolved oxygen in the feedwater. An oxygen scavenger, such as catalyzed sodium sulfite, should then be fed to react with the residual feedwater oxygen. Oxygen scavengers provide added protection not only to the boiler, but to the (after-boiler) steam and condensate system as well. Oxygen at levels as low as 0.005 mg/L can cause oxygen pitting in the steam and condensate system if not chemically reduced by oxygen scavengers.

Most of the corrosion damage to boilers and associated equipment occurs during idle periods. The corrosion is caused by the exposure of wet metal to oxygen in the air or water. For this reason, special precautions must be taken to prevent corrosion while boilers are out of service.

Wet Boiler Lay-Up. This is a method of storing boilers full of water so that they can be returned to service. It involves adding extra chemicals (usually something to increase alkalinity, an oxygen scavenger, and a dispersant) to the boiler water. Along with the boiler water additives, vapor-phase corrosion inhibitors can also be used for wet storage (lay-up). The water level is raised in the idle boiler to eliminate air spaces, and the boiler is kept completely full of treated water. Superheaters require special protection. Nitrogen gas can also be used on airtight boilers to maintain a positive pressure on the boiler, thereby preventing oxygen in-leakage.

Dry Boiler Lay-Up. This method of lay-up is usually for longer boiler outages. It involves draining, cleaning, and drying the boiler. A material that absorbs moisture, such as hydrated lime or silica gel, is placed in trays inside the boiler. Vapor-phase corrosion inhibitors can also be used for dry storage (lay-up). The boiler is then sealed carefully to keep out air. Periodic inspection and replacement of the drying chemical are required during long storage periods.

Boiler Blowdown Control

As a steam boiler produces steam, the dissolved and suspended solids, as well as the nonvolatile treatment chemicals, stay in the boiler (bulk water) itself. As more steam is produced and feedwater is introduced, the concentration of these dissolved and suspended solids will increase. As this concentration increases, sludge formation potential is increased. The increased concentration of alkalinity and other dissolved minerals decreases boiler water surface tension. This leads to the formation of water droplets that can carry over with the steam, causing wet steam. Wet steam has a lower energy content than dry steam, leading to an increase in the steam system operating cost. Wet steam can also lead to water hammer, erosion corrosion of the steam network, and increased cycles on steam traps.

There are two types of boiler blowdown: (1) **continuous (or surface) blowdown**, and (2) **manual (or bottom) blowdown**. Continuous blowdown uses a calibrated valve and a blowdown tap near the boiler water surface. As the name implies, it continuously takes water from the top of the boiler (just beneath the surface water level) at a predetermined rate. Continuous blowdown is generally an add-on feature and is not included on all boilers. However, by code (ASME 2015), all steam boilers must include a means for manual (bottom) blowdown. Manual blowdowns allow for the removal of solids that settle at the bottom (mud-drum or belly) of the boiler.

Dissolved solids tend to concentrate near the water surface in the steam drum. Therefore, surface blowdown is most effective in reducing the concentration of dissolved solids. Bottom blowdown is used to remove precipitated sludge from the boiler mud drum. However, blowdown results in the loss of heated water and treatment chemicals. Economical operation requires careful control of blowdown to maintain safe solids levels, while minimizing both heat and chemical additive losses.

There is no absolute rule for frequency of bottom blowdown. It can vary between once per shift to once or twice a week. The required frequency depends on the boiler, the feedwater quality and the type of chemical treatment program. A precipitating treatment program reacts with hardness in the feedwater to form a sludge that must be removed through bottom blowdown. A solubilizing treatment program keeps hardness in solution and creates little in the way of sludge.

Contact the boiler manufacturer for the recommended blowdown procedures. If none are available, the following can be used as a general guide: Manual blowdown should be done with the boiler under a light load when possible. The blowdown valve nearest the boiler should be opened first. Note that this valve should be a quick-opening valve. The downstream valve should be opened slowly until the line is hot. The valve should then be opened at a steady rate to drop the water level in the sight glass by approximately 13 mm. The valve should then be closed quickly, making sure that the hand

wheel is backed off slightly from fully closed to relieve any potential strain on the valve packing. The valve nearest the boiler should then be closed.

Controlling the continuous blowdown rate is important to prevent the problems associated with high dissolved and suspended solids, while minimizing the amount of water energy and treatment (waste) being sent to drain. Automated boiler blowdown controllers can measure the conductivity of the boiler water (a proxy for total dissolved solids), and control blowdown valves to maintain the correct boiler water cycles of concentration. These systems also have data-logging capability and communication functionality with cloud-based applications and building automation systems.

Steam and Condensate Network

Two other problems associated with steam and condensate systems include general corrosion and pitting corrosion. Naturally occurring alkalinity in the boiler water breaks down to carbonates, bicarbonates, and carbon dioxide (CO₂). The CO₂ leaves with the steam. As the steam water condenses, it dissolves some of the CO₂ to form carbonic acid, lowering the condensate pH. To prevent condensate corrosion, the systems must be protected from acidic conditions, which lead to general corrosion, and oxygen, which leads to pitting corrosion. Protection can be by mechanical or chemical means or a combination of both. The following methods are commonly used for condensate system protection.

Protection from General Corrosion.

Mechanical Protection. Reduce alkalinity from boiler feedwater to minimize the amount of carbon dioxide in the system. As discussed in the boiler water pretreatment section, alkalinity can be reduced by dealkalization, demineralization, and reverse osmosis. Note that in many cases, mechanical reduction of alkalinity is not needed because of low-alkalinity makeup water and/or feedwater.

Chemical Protection. Feed volatile neutralizing amines to the boiler system. Neutralizing amines are high-pH chemicals that neutralize the carbonic acid formed in the condensate (acid attack). The three most commonly used neutralizing amines are morpholine, diethylaminoethanol (DEAE), and cyclohexylamine. Neutralizing amines cannot protect against oxygen attack; however, they help keep oxygen less reactive by maintaining an alkaline pH. Neutralizing amines may be fed to the storage section of the deaerating heater, directly to the boiler with the internal treatment chemicals, or into the main steam header. Some steam distribution systems may require more than one feed point to allow proper distribution. Neutralizing amines are usually fed based on maintaining the condensate system pH > 8 and measured corrosion rates. These amines may be fed neat (undiluted), diluted with condensate or demineralized water, or mixed in low concentrations with the internal treatment chemicals. Different amines will have different basicity, neutralizing capacity, and distribution ratio. The proper blend is critical to ensure protection of the entire steam and condensate system, especially in larger and more complex buildings and campuses.

Protection from Oxygen Corrosion.

Mechanical Protection. Reduce oxygen from all boiler feedwater to prevent oxygen carryover to the steam and condensate system (via mechanical methods and chemical oxygen scavengers).

Chemical Protection. Feed filming amines to the steam to form a thin, hydrophobic barrier (film) on the condensate system surfaces. Filming amines are various chemicals that form a protective layer on the condensate piping to protect it from both oxygen and acid attack. The two most common filming amines are octadecylamine (ODA) and ethoxylated soya amine (ESA). The filming

amines should be continuously fed into steam headers at points that allow proper distribution. Combining neutralizing and filming amines is a successful alternative to protect against both acid and oxygen attack.

Chemical Protection. Feed a volatile oxygen scavenger to the steam to scavenge the oxygen. The need for chemical treatment can be reduced by designing and maintaining tight return systems so that the condensate is returned to the boiler and less makeup is required in the boiler feedwater. The greater the amount of makeup, the more the system requires increased chemical treatment.

Boiler Water Treatment Chemical Feed Methods

A properly designed water treatment program should be automated to feed the appropriate amounts of treatment proportional to the varying loads of the steam system. Meter-initiated chemical feed pumps or more complex control packages with chemical level feedback mechanism should be considered. Proper injection points for treatment chemicals are important in attaining optimal results from the water treatment program. The chemical handling, delivery, and disposal of containers must be considered. On-site mixing of chemicals should be avoided. Chemicals should be fed directly from preblended shipping containers or from microbulk double-wall containment tanks that are refilled by the water treatment vendor.

8. SELECTION OF WATER TREATMENT

As discussed in previous sections, many methods are available to prevent or correct water-caused problems. Selection of the proper water treatment method, and the chemicals and equipment necessary to apply that method, depends on many factors. The chemical characteristics of the water, which change with the operation of the equipment, are most important. Other factors contributing to the selection of proper water treatment are

- Economics
- Chemistry control mechanisms
- Dynamics of the operating system
- Design of major components (e.g., the cooling tower or boiler)
- Number of operators available
- Training and qualifications of personnel
- Preventive maintenance program

Once-Through Cooling-Water Systems

Economics is an overriding concern in treating water for once-through systems (in which a very large volume of water passes through the system only once). Protection can be obtained with relatively little treatment per unit mass of water, because the water does not change significantly in composition while passing through equipment. However, the quantity of water to be treated is usually so large that any treatment other than simple filtration or the addition of a few milligrams per litre of a polyphosphate, silicate, or other inexpensive chemical may not be practical or affordable. Intermittent treatment with polyelectrolytes can help maintain clean conditions when the cooling water is sediment laden. In such systems, it is generally less expensive to invest more in corrosion-resistant construction materials than to attempt to treat the water.

Open Recirculating Cooling-Water Systems

In an open recirculating system with chemical treatment, more chemical must be present, because the water composition changes significantly by evaporation. Corrosive and scaling constituents are concentrated. However, treatment chemicals also concentrate by evaporation; therefore, after the initial dosage, only moderate dosages maintain the higher level of treatment needed. The selection of a water treatment program for an open recirculating system depends on the following major factors:

- Economics
- Water quality
- Performance criteria (e.g., corrosion rate, bacteria count, etc.)
- System metallurgy
- Available staffing
- Automation capabilities
- Environmental requirements
- Water treatment supplier

An open recirculating system is typically treated with a scale inhibitor, corrosion inhibitor, oxidizing biocide, nonoxidizing biocide, and possibly a dispersant. The exact treatment program depends on the previously mentioned conditions. A water treatment control scheme for a cooling tower might include

- Chemistry and cycles of concentration control using a conductivity controller
- Alkalinity control using automatic injection of sulfuric acid based on pH
- Scale control using contacting water meters, proportional feed, or traced control technology
- Oxidizing biocide control using an ORP (oxidation-reduction potential) controller
- Nonoxidizing biocide control using timers and pump systems

Air Washers and Sprayed-Coil Units

A water treatment program for an air washer or a sprayed-coil unit is usually complex and depends on the purpose and function of the system. Some systems, such as sprayed coils in office buildings, are used primarily to control temperature and humidity. Other systems are intended to remove dust, oil vapor, and other airborne contaminants from an airstream. Unless the water is properly treated, the fouling characteristics of the contaminants removed from the air can cause operating problems.

Scale control is important in air washers or sprayed coils providing humidification. The minerals in the water may become concentrated (by evaporation) enough to cause problems. Inhibitor/dispersant treatments commonly used in cooling towers are often used in air washers to control scale formation and corrosion. Suitable dispersants and surfactants are often needed to control oil and dust removed from the airstream. The type of dispersant depends on the nature of the contaminant and the degree of contamination. For maximum operating efficiency, dispersants should produce minimal amounts of foam.

Control of slime and bacterial growth is also necessary in the treatment of air washers and sprayed coils. The potential for biological growth is enhanced, especially if the water contains contaminants that are nutrients for the microorganisms. Because of variations in conditions and applications of air-washing installations and the possibility of toxicity problems, individual treatment options should be discussed with water treatment experts before a program is chosen.

Closed-Loop (Hot/Chilled) Recirculating Systems

Closed recirculating systems or closed hydronic loops use a water-based solution to transfer heat. The most common distinction defining a closed system is the fact that the method of cooling is nonevaporative. Minimal water loss/makeup and minimal air contact are two additional conditions typically associated with closed loops. Closed systems are so diverse in application that it can be difficult to suggest a standard set of operating conditions and design.

In a closed recirculating system, water composition remains fairly constant, with very little loss of either water or treatment chemical. Closed systems are often defined as those requiring less than 5% makeup per year. The need for water treatment in such systems (i.e., water heating, chilled water, combined cooling and heating, closed-loop condenser water systems) is often ignored based on

the rationalization that the total amount of scale from the water initially filling the system would be insufficient to interfere significantly with heat transfer, and that corrosion would not be serious. However, leakage losses are common, and corrosion products can accumulate sufficiently to foul heat transfer surfaces. Therefore, all systems should be adequately treated to control corrosion. Systems with high makeup rates should be treated to control scale as well.

The selection of a treatment program for closed systems should consider the following factors:

- Economics
- System metallurgy
- Operating conditions
- Makeup rate
- System size

Before new systems are treated, they must be cleaned and flushed. Grease, oil, construction dust, dirt, and mill scale are always present in varying degrees and must be removed from the metallic surfaces to ensure adequate heat transfer and to reduce the opportunity for localized corrosion. Detergent cleaners with organic dispersants are available for proper cleaning and preparation of new closed systems.

Some of the most serious corrosion damage is done to new systems because of improper start-up procedures. In almost all cases, this problem is caused by filling a system with untreated water for the purpose of performing pressure tests. Typically, the system is then left stagnant, sometimes for many months, until it is ready to be commissioned. During that time, oxygen corrosion, underdeposit corrosion, and microbiologically influenced corrosion will waste system metals, sometimes to a considerable degree.

New systems should never be filled with untreated water, and even when treated should not be left stagnant for long periods of time. In addition, new systems should be thoroughly cleaned and flushed with an appropriate pretreatment chemistry as early as possible, preferably with the initial filling. Attending chemical company recommendations should be followed on the cleaning and flushing procedure.

After a system has been cleaned and thoroughly flushed of pretreatment chemicals, it should be immediately refilled with water and treated with the recommended corrosion inhibitor and microbiological control products. The system should not be allowed to sit empty for any length of time, unless extraordinary effort is made to ensure that it is completely dry.

Corrosion-inhibiting treatments for closed water systems are usually composed of several constituents and typically contain molybdate, nitrite, or other inhibitor compounds as a control parameter. The chemical manufacturer's recommendations should be followed as to the amount of inhibitor that should be maintained in the system.

HVAC Closed Loops Containing Aluminum (Mixed-Metallurgy Systems)

These loops must be treated primarily to control corrosion and sometimes biological fouling, but may also need cleanup programs to remove new or old corrosion products.

There are several important water treatment issues that must be addressed in a mixed-metallurgical system:

- The pH must be considered for amphoteric metals, such as aluminum and zinc, that can corrode in both acid and alkaline pHs. Manufacturer's specifications should be followed.
- Free copper should generally be maintained <0.1 mg/L with a copper inhibitor.
- Total aerobic bacteria counts should be controlled to less than 100.0 colony-forming units per millilitre (cfu/mL).

- Mixed-metallurgy corrosion inhibitors should contain appropriately dedicated corrosion inhibitors for the mixed metals of the system.

All closed loops need a mechanism to introduce chemicals into the system. Pot feeders are the most common tool used for this application, but chemical pumps can also be used to introduce the chemicals. Use caution not to increase the system pressure to a point the pressure relief valve opens.

Newer systems or pot feeder replacements should use filter/feeders. These units have a stainless steel sleeve strainer that is inserted into the specially designed pot feeder that allows the unit to become a filter once a filter bag is added. Filtration can occur down to sub-micron (<0.5 μm) levels.

Corrosion Coupon Racks. Closed loops should be outfitted with a two- to four-position corrosion coupon rack with a rotameter (visual flow indicator) to verify that the flow rate through the rack is appropriate and representative of the system: generally 0.9 to 1.5 m/s. This is equivalent to 30 to 50 L/min for a 25 mm coupon rack and 19 to 34 L/min for a 20 mm coupon rack.

Water Meters. Each closed-loop system should be outfitted with a water meter to measure the amount of water fed into the system. A log of the readings should be kept; this helps in detecting leaks.

Filtration. When filtration is needed, the easiest solution for smaller systems is replacing the pot feeder with a filter feeder. Filtration down to 5 μm size is desirable; however, dirty systems should start with >25 μm size filtration to allow a gradual removal of suspended solids. The optimum size can be determined by a particle size distribution analysis. Pressure gages and a flow meter at the filter outlet should be placed on the filter unit to help identify when the bags, cartridges, or media need to be changed or cleaned, based on the inlet and outlet pressure differentials. Aluminum condensing boilers need filtration because of (1) their high ratios of metal surface to water volume and (2) their ribbed and textured aluminum alloy surfaces required for efficient heat transfer.

Glycol Systems. Glycol systems are closed-loop water systems that usually contain over 20% (by mass) of either propylene glycol or ethylene glycol (solution also known as antifreeze). In geothermal cooling and heating systems, this is usually a mixture of water and alcohol (typically ethanol rather than methanol or propanol, because ethanol is safer than methanol and has lower freeze point and viscosity than propanol). For most HVAC applications, inhibited nontoxic propylene glycol replaces inhibited toxic ethylene glycol as antifreeze and for burst protection. It is commonly used as an all-year coolant in closed evaporative cooler circuits, and in chilled- and hot-water circuits that are exposed to freezing temperatures. To protect against freezing during seasonal lay-ups, it is charged at the end of a cooling season into parts of closed water systems that are vulnerable to burst failures from freezing.

These vulnerable system parts are isolated and filled with 20 to 40% glycol in fall before seasonal shutdown to prevent freezing. They are then drained and flushed before summer startup to resume normal operation. Inhibited glycol, when diluted to below 20%, loses its antiseptic and pH stabilizing (buffering) abilities, turns acidic after decomposition by oxygen and heat, becomes corrosive to metals, and can be a food source for microbes. Most glycol manufacturers recommend keeping inhibited glycol above 25% concentration. Flushing without testing for trace glycol can lead to trace glycol contamination, which can cause high turbidity, corrosiveness, and repulsive odor. See [Tables 3](#) and [4](#) for data on glycol and freeze protection.

Treatment of antifreeze systems is similar to treating closed-loop water systems. It requires pretreatment (start-up) cleaning with alkaline low-foaming detergent. When aluminum and/or galvanized steel are present, chemically neutral low-foaming detergent is used

Table 3 Percent Glycol by Mass Versus Freezing Point

% Glycol, by Mass	Freezing Point, °C	
	Ethylene Glycol	Propylene Glycol
0	0	0
5	-1.4	-1.6
10	-3.2	-3.3
15	-5.4	-5.1
20	-7.8	-7.1
25	-10.7	-9.6
30	-14.1	-12.7
35	-17.9	-16.4
40	-22.3	-21.1
45	-27.5	-26.7
50	-33.6	-33.5
55	-41.1	-51.1

Table 4 Freeze and Burst Protection by Volume

Temperature, °C	Ethylene Glycol, % by Volume		Propylene Glycol, % by Volume	
	Freeze	Burst	Freeze	Burst
-6.7	17.3	11.9	18.0	12.0
-12.2	27.1	18.4	29.0	20.0
-18	25.7	23.8	36.0	24.0
-23.3	42.2	28.1	42.0	28.0
-28.9	47.6	32.5	46.0	30.0
-34.4	51.9	32.5	50.0	33.0
-40.0	56.3	32.5	54.0	35.0
-45.6	60.6	32.5	57.0	35.0

to protect those metals. Phosphate-based detergent is also preferred over silicate base, because residual silicate can become a source of foulants to the piping when pH turns from neutral to acidic. In addition to controlling freezing points with different concentrations of antifreeze, corrosion is controlled with either demineralized makeup water or preblended inhibited glycol fed with an automatic antifreeze (glycol) feeder. The arrangement can stop raw makeup water from entering the system, upsetting glycol concentrations and diluting inhibitor levels. Makeup water quality with total hardness <50 mg/L as CaCO₃, chloride as Cl <25 mg/L, and sulfate as SO₄ <25 mg/L is preferred for control of corrosion. When inhibitor levels are out of balance, inhibitors may be fed with a bypass filter feeder to control pH, alkalinity, turbidity, and copper and ferrous inhibitors levels. The bypass feeder serves as a sidestream filter to remove suspended metal oxides. An inhibitor program protects multimetal materials, steel, cast iron, copper, brass, aluminum, and solder with buffered pH between 8 and 10.5; phosphates are common buffering agents with concentrations between 2000 and 4000 mg/L. Nitrite borate and silicate are less preferred because of potential for unfavorable reactions with glycol.

Water-Heating Systems

Secondary and Low Temperature. Closed, chilled-water systems that are converted to secondary water heating during winter and primary low-temperature water heating, both of which usually operate in the range of 60 to 120°C, require sufficient inhibitors to control corrosion. For more information on treatment selection for these systems, see the section on Corrosion and Corrosion Control.

Environment and High Temperature. Ambient-temperature water-heating systems (120 to 175°C) and high-temperature, high-pressure hot-water systems (above 175°C) require careful consideration of treatment for corrosion and deposit control. Makeup water for such systems should be demineralized or softened to prevent scale deposits. For corrosion control, oxygen scavengers such as sodium sulfite can be added to remove dissolved oxygen.

Electrode boilers are sometimes used to supply low- or high-temperature hot water. Such systems use heat generated from the electrical resistance of the water between electrodes. The conductivity of the recirculating water must be in a specific range depending on the voltage used. Treatment of this type of system for corrosion and deposit control varies. In some cases, oil-based corrosion inhibitors that do not contribute to the conductivity of the recirculating water are used.

Thermal Storage Systems

Thermal storage systems require the same attention as other systems as it relates to corrosion, scale, and biological control. As with other systems, it is important to begin with a clean system. The system should be properly cleaned and passivated after construction and before operation and then treated with appropriate corrosion inhibitors and biocides. The large volume typical of thermal storage systems can result in periodically stagnant conditions and solids accumulation. The system should be equipped with a filter to facilitate solids removal. Either a physical or instrumental method of corrosion monitoring should also be used to ensure that acceptable corrosion rates are achieved.

Brine Systems

Systems containing brine, a strong solution of sodium chloride or calcium chloride, must be treated to control corrosion and deposits. Sodium nitrite, at a minimum 3000 mg/L in calcium brines or 4000 mg/L in sodium brines, and a pH between 7.0 and 8.5, should provide adequate protection. Organic inhibitors are available that may provide adequate protection where nitrites cannot be used. Molybdates should not be used with calcium brines because insoluble calcium molybdate will precipitate.

Nonchemical and Physical Water Treatment Methods

Water treatment equipment based on physical properties of water has been used for boiler water, cooling water, and other process applications for decades. Continued development has yielded multiple classifications of such treatment methodologies and equipment systems. The adherence to manufacturers' recommendations and the proper application of these technologies is critical to achieving successful results. As with traditional methods of water treatment, the ability to achieve successful results should be adequately evaluated for the water treatment system as well as regularly monitored for effective control of scale, corrosion, and biological contamination. All water treatment (program) technologies, published papers, and case histories should be evaluated in light of water supply chemistry, operating environment, duty, and industry standard performance metrics.

A number of nonchemical and physical water treatment equipment technologies are classified in the following paragraphs, along with brief summaries of their basic claims and theoretical mechanisms of action.

Magnetic or fixed-field magnetic systems are designed to cause scale-forming minerals to precipitate on suspended solids as opposed to heat exchanger surfaces. This mechanism produces nonadherent particles, often classified as the aragonite form of calcium carbonate versus the hard, adherent calcite. The precipitated particles can then be removed by blowdown, mechanical means, or physical flushing.

Electromagnetic systems induce a constant or variable magnetic flux density (or both), thereby inducing a localized, variable electric field in the bulk water. **Pulsed-power** and **electrodynamic** field systems generate a combination of variable magnetic flux density with a variable electric field at frequencies greater than the incoming line signal. The induced electric fields alter the surface charge on suspended solids and particulate and force precipitation on these surfaces in the bulk water.

Cavitation systems can cause the formation and sudden collapse of low-pressure bubbles in a water stream by means of a mechanical force. The collapse of the bubbles imparts a shock wave and resultant heat locally within the water flow. The energy created during the implosion of bubbles promotes precipitation of minerals in the water stream.

Ionization rods create a static electric field that disperses scale-producing foulants, thereby inhibiting precipitation of minerals on equipment surfaces. Inhibition of biological growth is also due to the dispersion process initiated by the electric field created by these devices.

Electrolysis systems pass an electric current between two electrodes. Precipitation of minerals occurs at the cathode. Inhibition of biological growth is accomplished by formation of chlorine gas at the anode; the gas combines with water to form hypochlorite.

Ultrasonic systems impart high-frequency sonar energy in the ultrasonic range to a stream of water. The sound wave produced by ultrasonic devices can cause mechanical damage to bacteria cell walls. Similar to cavitation devices, ultrasonic energy can also produce low-pressure bubbles, which can collapse and contribute to the damaging of bacteria cell walls.

Ultraviolet light systems irradiate a water stream with ultraviolet light. Exposing microorganisms to ultraviolet light can inhibit their biological growth. The ability to effectively and efficiently control microbial populations throughout a cooling-water system solely by irradiating a water stream with a point-of-use ultraviolet light system must be evaluated for a given system.

Ozone systems stream ozone created by coronal plasma, by ultraviolet lamps, or by chemical reaction, into the bulk water. When contact is made with microorganisms, ozone can be a very effective disinfectant for their control. However, it is difficult to maintain an effective residual of ozone throughout a cooling-water system because of its high reactivity and fast dissipation. Ozone is very volatile and can be lost from the system as the water passes through the cooling tower fill. Successful application of ozone for biological control requires that sufficient ozone-generating capacity be provided to sustain a level of ozone residual that will control microbial contamination throughout the cooling-water system.

ASHRAE research projects RP-765 (Nasrazadani and Chao 1996) and RP-747 (Gan et al. 1996) found ozone only marginally effective as a scale and corrosion inhibitor, respectively. Ozone has been shown to have a very limited and unpredictable effect on calcium carbonate scale. Ozone has also been shown to have a limited effect to inhibit corrosion of most metals. It provides some reduction of mild steel corrosion, but increases the corrosion rates of copper and copper alloys. It is also known to attack galvanized steel, and increasing the level of ozone in water increases the corrosiveness of the water.

ASHRAE research project RP-1155 (Cho 2002) studied physical water treatment with respect to scale prevention and/or mitigation. For the study, a physical water treatment (PWT) device was defined as a nonchemical method of water treatment for scale prevention or mitigation. Bulk precipitation on colloidal surfaces was proposed as the mechanism of scale prevention. Three different PWT devices (permanent magnets, a solenoid coil device, and a high-voltage electrode) were tested under laboratory conditions. Fouling resistance data obtained in a heat transfer test section supported the benefit of all three devices when configured in optimum conditions in the laboratory-scale test system.

ASHRAE research project RP-1361 (Vidic et al. 2010) studied physical water treatment and microbial control. In this study, a PWT device was defined as a nonchemical method of water treatment for microbial control. Five different PWT devices (magnetic, pulsed electric field, electrostatic, ultrasonic, and hydrodynamic cavitation) were tested in a pilot-scale cooling tower. No statistically significant difference in planktonic and sessile microbial concentra-

tions was observed in the (test) pilot-scale cooling tower for any of the devices, as compared to an untreated control tower.

9. TERMINOLOGY

The following terms are commonly used in the water treatment industry as they pertain to corrosion, scale, deposit, fouling, and microbiological control.

Alkalinity. The sum of bicarbonate, carbonate, and hydroxide ions in water. Other ions, such as borate, phosphate, or silicate, also contribute to alkalinity.

Anion. A negatively charged ion of an electrolyte that migrates toward the anode influenced by an electric potential gradient. Common examples are chloride (Cl^{-1}), sulfate (SO_4^{-2}), bicarbonate (HCO_3^{-1}), carbonate (CO_3^{-2}), and phosphate (PO_4^{-3}).

Anode. The positive electrode of an electrolytic cell at which oxidation occurs.

Biological deposits. Water-formed deposits of biological organisms or the products of their life processes. Examples include barnacles, algae, or bacterial slime (biofilm).

Cathode. The negative electrode of an electrolytic cell at which reduction occurs.

Cation. A positively charged ion of an electrolyte that migrates toward the cathode influenced by an electric potential gradient. Common examples are calcium ion (Ca^{+2}), magnesium ion (Mg^{+2}), sodium ion (Na^{+1}), potassium ion (K^{+1}), and ferric iron (Fe^{+3}).

Corrosion. The deterioration of a material, usually a metal, by reaction with its environment.

Corrosivity. The capacity of an environment or environmental factor to bring about destruction of a specific metal or material by the process of corrosion.

Electrolyte. A solution through which an electric current can flow. Water without ions present in it will not conduct electricity. Ions dissolved in water create an electrolyte and allow current to flow. The more concentrated the ions, the easier it is for current to flow.

Filtration. Process of passing a liquid through a porous material in such a manner as to remove suspended matter from the liquid.

Galvanic corrosion. Corrosion resulting from the contact of two dissimilar metals in an electrolyte or from the contact of two similar metals in an electrolyte of nonuniform concentration.

Hardness. The sum of the calcium and magnesium ions in water; usually expressed in mg/kg or mg/L as CaCO_3 .

Inhibitor. A chemical substance that reduces the rate of corrosion, scale formation, fouling, or slime production.

Ion. An electrically charged atom or group of atoms.

Passivity. The tendency of a metal to become inactive in a given environment. "Noble" metals such as gold, silver, and platinum are inherently passive or unreactive with respect to water. Water reactive ("active") metals such as iron, aluminum, nickel, and zinc acquire varying degrees of passivity because of natural and inhibitor-enhanced formation of an extremely thin, protective oxide surface film.

pH. The logarithm of the reciprocal of the hydrogen ion concentration of a solution. pH values below 7 are increasingly acidic; those above 7 are increasingly alkaline.

Polarization. The deviation from the open circuit potential of an electrode resulting from the passage of current. Also used to describe the absence of electron flow where corrosion of an active metal is possible.

ppm. Parts per million by mass. In water, ppm are essentially the same as milligrams per liter (mg/L); 10 000 mg/L = 1%.

Scale. (1) The formation at high temperature of thick corrosion product layers on a metal surface. (2) The precipitation of water-insoluble constituents on a surface.

Sludge. A sedimentary water-formed deposit, originating from (1) biological sources, (2) capture of suspended particles from the air, and/or (3) in-system formation hardness or corrosion debris.

Tuberculation. The formation over a surface of scattered, knob-like mounds of localized corrosion products.

Water-formed deposit. Any accumulation of insoluble material derived from water or formed by the reaction with water on surfaces in contact with it.

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