

CHAPTER 50. WATER TREATMENT: DEPOSITION, CORROSION, FOULING, AND BIOLOGICAL CONTROL

THIS chapter covers the fundamentals of water treatment and conditioning. 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 extends the life of equipment in both open- and closed-loop systems. Water treatment helps conserve water resources as well as enable the use of alternative sources of water. These benefits help to promote a healthier, more sustainable environment.

1. WATER QUALITY AND ITS SOURCES

1.1 WATER CHARACTERISTICS

Water 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 water vapor and steam at atmospheric pressure. Steam can carry large quantities of heat. Such qualities position water as the ideal material for heating, cooling, and power generating processes.

Water supplies contain varying amounts of impurities that can lead to scale formation, corrosion, and other problems in industrial equipment. Starting with rain, water accumulates impurities from its surroundings, dissolving minerals and picking up various substances from the air, soil, vegetation, and other materials. For this reason, water is often referred to as the **universal solvent**. Falling rain dissolves carbon dioxide and oxygen from the atmosphere. As carbon dioxide breaks up in water, it forms carbonic acid (H_2CO_3). When carbonic acid contacts soil or rock strata containing limestone (CaCO_3), it slowly dissolves the calcium to form highly soluble calcium bicarbonate. This process occurs in soil or rock strata where temperatures are relatively cool (less than 21°C). Unfortunately, bicarbonate does not remain stable as water warms, and the limestone dissolution can be quickly reversed to reform calcium carbonate when hard water is heated. Calcium carbonate that reforms 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 the need for equipment replacement.

Water's composition can change 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 the impurities in water may act to corrode the metal equipment containing it. The actions of water in HVAC systems depend on the types of impurities and the temperatures and pressures to which it is subjected, among other factors.

The following definitions present the most relevant chemical and physical terms, properties or characteristics of water relevant to water treatment and that affect its use in HVAC and other applications.

Parts per million (ppm) is a dimensionless ratio, used in water treatment to express concentration (e.g., one gram in a million grams, one mL per L). Dissolved minerals and impurities commonly found in water are present at very low concentration (e.g., milligrams in a full glass of water). The most convenient ratio to express concentration is then milligrams per million milligrams, or milligrams per litre (L), of water (the mass of a litre of water is almost equivalent to 1,000,000 milligrams). In water treatment, ppm concentration is almost always expressed in mg/L.

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 the potential for formation of hard calcium and magnesium carbonate scales, such as those found in improperly treated boilers and cooling-water systems. Harder water contributes to scale formation because heating encourages deposition of calcium carbonate, or lime scale. Solubility of most calcium and magnesium salts decreases with an increase in temperature, so these salts tend to form scale on heat transfer surfaces where the metal skin temperature is greater than the bulk water temperature. Boiler and cooling-water treatment programs are designed to control deposition of hardness salts through pretreatment removal of hardness (e.g., water softening by ion exchange) or internal chemical additive conditioning to solubilize, remove by precipitation, or otherwise control deposition.

Alkalinity is a measure of the capacity of water to neutralize strong acids and bases, defined in a specific water testing procedure. This procedure uses a measurable amount of a dilute acid solution of known concentration to change the color of two specific indicators, phenolphthalein and methyl orange. Alkalinity of near-neutral pH water is the measured carbonate and bicarbonate minerals (calculated as calcium carbonate [CaCO_3]), and refers to the primary

alkaline earth minerals. Alkalinity of alkaline water also includes hydroxide ions (OH^-), when present. All natural waters contain some alkalinity. The presence of alkalinity contributes to scale formation, because it can contribute carbonate ions, driving formation of calcium carbonate. In natural waters, 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. [Table 1](#) allows calculations of different alkalinities to monitor and control water quality.

Alkalinity is measured using two different pH end-point indicators. The **phenolphthalein alkalinity (P alkalinity)** measures the strong alkali present, including carbonate and hydroxide at pH 8.3, and the **methyl orange alkalinity (M alkalinity)**, or **total alkalinity**, measures the total alkalinity in the water at pH 4.3. Note that total alkalinity includes the phenolphthalein alkalinity. For most natural waters, the actual chemical species present can be estimated after performing two specific alkalinity tests. Treated waters may also include the hydroxide alkalinity contributed by OH^- ([Table 1](#)). For water systems treated with glycol, reserved alkalinity is used to indicate its ability to resist reduction of pH. See the Terminology section for its definition.

Table 1 Alkalinity Relationship Based on P and M Tests

Situation	Hydroxyl	Level of Alkalinity 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

pH is a measure of the concentration of hydrogen ions (the acid strength) of a solution. Mathematically, it is defined as the negative logarithm of the hydrogen ion concentration (pH of 1 is very acidic; pH of 14 is very basic; a pH of 7 is 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 water systems depend on either pH control or maintaining pH above a specified minimum level. Unexpected changes in pH (~1.0 to 1.5 pH increase or decrease) are usually indications of events that need corrective actions.

Chlorides are the total of dissolved chloride components of salts such as sodium chloride, potassium chloride, calcium chloride, magnesium chloride, etc. Sodium chloride (NaCl) and calcium chloride (CaCl_2) are the most common chloride salts found in water. Chlorides do not ordinarily contribute to scale, because they are very soluble. However, chlorides are corrosive and can be excessively so when present in high concentration, as in seawater, because of their ability to react with and weaken the natural protective oxide films present on most metals. Determining the concentration of chlorides in water is useful in evaporative systems for determining cycles of concentration. Most water constituents change in concentration when common treatment chemicals are added or due to chemical changes that take place in normal operation. Chlorides are not affected by such changes, so, with few exceptions, only evaporation affects chloride concentration. Therefore, 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 treated with chemicals releasing chloride.)

Conductivity, or specific conductance, measures the ability of water to conduct electrical current and act as an electrolyte. Conductivity increases with an increase in total dissolved solids (ions) present in the water. Conductivity is the reciprocal of specific resistance at 25°C and can be used to estimate total dissolved solids.

Dissolved solids consist of soluble salts, including water hardness, and other materials that combine with water as a solution. They can affect the formation of corrosion and scale. Total dissolved solids are referred to as **TDS** and is most commonly determined based on the electrical conductivity of water. Dissolved solids can also be determined by the weight of the dried residue after water, filtered through a 0.45 μm filter, is totally evaporated from a sample.

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 (homogeneously suspended). Naturally occurring compounds such as lignin and tannins are often colloidal. At high velocities, hard suspended particles can abrade equipment. Settled suspended matter of all types can contribute to under-deposit corrosion, as it fosters corrosive microbiology. Total suspended solids larger than 1.5 μm are referred to as TSS and do not include TDS.

Silica is dissolved sand or silica-bearing rock (such as quartz). 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. It can exist in reactive (ionic) and unreactive (colloidal) forms. Fortunately, silicate deposition is less common than other deposits. Silica can vaporize in high-pressure steam boilers to cause hard adherent deposits in steam turbines when cooled.

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. Their presences is the product of the dissolution of sulfate-bearing rock, such as gypsum. Calcium and magnesium sulfate scales are very hard, are difficult to remove, and greatly interfere 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 is the amount of opacity caused by suspended matter and is often described as cloudiness or haziness in water. It should not be confused with color. Water may be dark in color but still clear and not turbid. Turbidity is caused by suspended matter, in a finely divided state, which can scatter and deflect incoming light. Clay, silt, organic matter, microscopic organisms, and similar materials are common causes of turbidity. Although suspended matter and turbidity are closely related, they are not synonymous. Suspended matter is the quantity of insoluble material of $>1.5\ \mu\text{m}$ in water that can be removed by filtration. Levels of suspended matter and turbidity will likely change based on the dynamics of water flow or lack of flow. Turbidity of water used in HVAC systems should be as low as possible, particularly for steam boiler feedwater. Turbidity includes submicron particles and can concentrate in the boiler and settle as sludge or mud. It can also cause increased boiler blowdown, plugging, overheating, priming, and foaming.

Biological matter such as bacteria, algae, fungi, protozoa, and shellfish can be present in water, and their growth in water systems can cause operating, maintenance, and health problems. Microbial growth should be assumed to 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, reduce heat exchanger (transfer) efficiencies, and cause microbial corrosion.

Holding time index (HTI) is defined as the half-life of added chemical in an open system. It is time required to decrease 50% of its initial concentration through measured bleed off or water losses. It is calculated by dividing system volume by the rate of system bleed off, or blowdown. HTI is reflective of the amount of aging within a system.

Dispersant is a term used to express an additive's ability to aid in suspending very small particles, so they do not readily agglomerate, settle, or adhere to surfaces. Dispersants are typically chain-like compounds (polymers) that can attach to and engulf very small particles. Dispersive polymers are designed to include areas of electrical negative charge to impart repulsive activity between polymer-engulfed particles. Short-chained polymers also have antiscaling and antifouling properties through distortion of scale-forming structures to render them nonadherent to contact surfaces.

1.2 WATER SOURCES

Municipal water sources in the United States are generally of high quality and in compliance with federal government (EPA and U.S. Public Health) standards as well as state and local requirements. Depending on the primary geographic source, water properties may be quite constant, as where water is drawn from the Great Lakes or fixed-strata deep wells. In contrast, some properties are quite variable, where water may be obtained from rivers, lakes, or wells as season and water demand dictate. Highly variable water properties can be particularly challenging in management of boiler and cooling tower treatment programs (e.g., obtaining desired response from treatment control equipment, maintaining proper function of water conditioning equipment such as water softeners, dealing with water that varies between being corrosive and being scale forming over time). Municipal supplies, though low in contaminants initially, can pick up iron corrosion debris from miles-long delivery mains leading to episodes of iron-rich "red water." Municipal water should also not be presumed microbiologically sterile. Water mains typically possess biofilm of significant thickness. Local water quality can also be impacted by heavy rains in an area, water main breaks, and maintenance on the distribution system, as well as distance from the water treatment plant, leading to a loss of disinfectant concentration.

Alternative Water Sources

Corporate, public, and private well sources of water may have lower quality, unstable consistency of chemical properties, or reliability of supply. In addition, issues of odor, taste, or turbidity may arise, and contaminants typically not found in municipally processed water may be present.

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 much more attractive. 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 substitute for fresh water. The economic and environmental payback of 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 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 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 issues related to environmental health, corrosion, scale, and microbiological growth.

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 varies considerably throughout the year. For example, a 3517 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% relative humidity (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.

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 significant. The need for cooling tower makeup and the availability of it from cooling coils are generally simultaneous, thus minimizing storage costs.

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

A typical rainwater recovery system directs rainwater from the roof to a storage tank rather than a storm sewer. This cache can then be used for various purposes throughout a facility, including irrigation and cooling tower makeup. 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. However, when it is exposed to roof activities (e.g., cooling tower blowdown, equipment cleaning, roof restaurant discharges), its quality can be unstable and require treatment. Once collected from a roof and filtered, it is disinfected with an oxidizing biocide to minimize biological growth and monitored before being used as cooling tower makeup water from the storage tank.

Reclaimed Water. Reclaimed water, or recycled water, is highly treated wastewater from a wastewater treatment plant. This nonpotable water source is delivered to a facility through purple or lavender 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, reclaimed water contains a higher concentration of hardness and alkalinity, which increases the tendency to form 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, such as 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. It is also corrosive to copper and copper alloy. Yellow metal corrosion inhibitors like azole must be kept high. Reclaimed water also has higher background bacteria levels than potable water. Because of the increased potential for biocorrosion and biofouling problems related to bacteria growth, additional biocides are usually required. A combination of oxidizing and nonoxidizing biocides usually works best.

The local water treatment facility can provide a reclaimed water quality report so the proper treatment program can be implemented. To guard against upsets in evaporative heat rejection systems, it is often recommended to use more corrosion-resistant materials of construction.

Blended Water. Blending one or more alternative water sources can 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 could be suitable with conditioning for use as tower makeup.

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 correctly blend two or more water supplies.

2. WATER TREATMENT

2.1 CONTROL

Deposition

Several different types of deposits can form in HVAC 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 or delay these 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. Microbiological fouling is slime or biofilm that accumulates by incorporating inorganic particulate matter such as calcium carbonate, silica, and corrosion products.

Scale is formed when the oversaturation of dissolved minerals creates deposits from the water onto heat transfer surfaces or pipes. As water evaporates in a cooling tower or steam boiler, the concentration of dissolved solids becomes greater, and the solubility of particular scale-causing mineral salts can be exceeded. When this situation occurs in a cooling- or steam-water system, scale may 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) magnesium silicate, usually in that order. Most salts are more soluble in hot water than in cold water; however, most calcium and magnesium salts, including calcium phosphate, calcium carbonate, and magnesium silicate, 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- and boiler-water systems. For instance, a layer of calcium carbonate scale as thin as 0.40 mm can reduce heat exchanger capacity by 15%.

Several key factors influence whether scale forms:

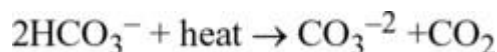
- Temperature
- pH
- Alkalinity
- Hardness (concentration of scale-forming salts)
- Total dissolved solids (influence of other dissolved materials, which may or may not be scale-forming)
- Phosphate-ortho
- Silicate/silica

As any of these factors changes, so do scaling tendencies. Changes in pH or alkalinity can greatly affect scale formation. For example, as pH or alkalinity increases, calcium carbonate becomes less soluble and deposits on surfaces.

Some materials, such as silica (SiO₂), 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.

Calcium Carbonate Formation (Hard Lime Scale)

The progression of calcium carbonate deposition and scale formation is fundamentally a reversal of the process of creating hard water (when carbonic acid in rainwater dissolves limestone). However, this bond is easily undone once water is put to practical use, because the bicarbonate component of hard water is thermally unstable:



Alkalinity breakdown produces carbonate ion and carbon dioxide (easily lost from a system as a gas). The percentage of bicarbonate broken down increases so long as heat continues to be added to water.

The solubility of calcium bicarbonate is more than 10 000 mg/L. The solubility of calcium carbonate at 24°C is roughly 10 mg/L: 4 mg/L calcium ions and 6 mg/L carbonate ions. Basic chemistry dictates that, for aqueous salts of limited solubility, any effort to increase the concentration of one constituent must cause the concentration of the other constituent to fall. Expressed mathematically, when a soluble salt such as calcium carbonate is dissolved in water, multiplying the concentration of each constituent produces a fixed number K_{sp} (or solubility product or constant).

Hard water typically contains roughly two bicarbonate ions (HCO_3^-) for every calcium ion (Ca^{2+}). Cooling tower and boiler makeup water supplies frequently hold up to 300 mg/L hardness or more, which may be further concentrated several times by evaporation in a cooling tower or boiler. Calcium and bicarbonate concentrations may easily approach several hundred mg/L each. Bicarbonate alkalinity breakdown can then lead to levels of 100 mg/L or greater of carbonate ions combined with a near equal concentration of calcium ions to form a very highly supersaturated solution of calcium carbonate, in violation of the solubility product limit.

Scale and sludge are not produced instantly when hard water is introduced into a cooling tower or boiler, because calcium carbonate precipitates only very slowly from a supersaturated solution of calcium and carbonate ions. Such supersaturated solutions are termed **metastable**, in that there is great potential for precipitation to occur, but induction time is required for its initiation, agglomeration, and adhesion to contact surfaces. For example, hotter heat transfer surfaces speed up initiation and promote formation of the densest crystal structure (calcite). Biofilm in cooling water systems can attract calcium and increase pH locally through protein decomposition (ammonization) to form calcium-carbonate-rich mud and sludge, and carbonate-rich deposits can form on cooling tower fill at wet/dry boundaries due to hypersaturation.

Deposition, Scale, and Suspended-Solids Control

HVAC system treatment strategy is dictated by makeup chemical properties and operating constraints. Treatment of cooling towers fed with makeup water of relatively low hardness is usually quite different than that for cooling towers fed with high-hardness makeup water. In some instances, local water resource conservation or discharge regulations may dramatically affect the treatment strategy used. Manufacturers' water quality specifications also affect water treatment strategy.

Steam and High-Temperature Heating Water:

- Makeup water conditioning:
 - Ion exchange (softeners and dealkalizers) to remove calcium, magnesium, and alkalinity.
 - Reverse osmosis (RO) to remove almost all dissolved solids including calcium and magnesium.
 - Deionization (DI) to remove all dissolved solids.
 - Deaeration to aid control of dissolved oxygen, carbon dioxide from carbonate species, and steam condensate pH.
- Internal chemical treatment of boiler water:
 - Various chemical additives such as sodium hydroxide, sodium carbonate, phosphates, dispersive agents, etc. may be added to "soften" boiler water internally via precipitation of hardness and blowdown, but this practice is considered out of date, and makeup water conditioning is favored. Chemical additives are typically used to address low level hardness not removed by makeup conditioning or due to external contamination.
- Maintain good internal boiler and steam condensate protection against corrosion to control iron deposition on internal boiler surfaces.

Cooling Towers:

- Makeup water conditioning:
 - Ion exchange (softening) to remove calcium and magnesium.
 - Reverse osmosis (RO) to remove almost all dissolved solids including calcium and magnesium.
 - Filtration to remove turbidity and suspended metals.
- Add acid to cooling tower water to remove alkalinity and control carbonate ion formation
- Add scale inhibitors and dispersants to dramatically slow rate of particle nucleation and agglomeration.

Scaling Indices

To help determine the tendency of water to form or dissolve calcium carbonate scale, several scaling indices have been developed. These indices are only for indicating the degree of saturation of calcium carbonate scale, not scale of other calcium compounds (such as calcium sulfate). These indices are calculated using the pH, alkalinity, calcium hardness, temperature, and total dissolved solids of the water.

Langelier Saturation Index (LSI). 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 **pH(s)** is calculated. Subtracting the water's pH(s) from its actual pH then

results in the LSI. If the water's measured pH (**pH [actual]**) is greater than its pH(s) (i.e., positive LSI value; oversaturation), the water has a scale-forming tendency. If the water's pH (actual) is less than its pH(s) (i.e., negative LSI value; undersaturation), the water will have a scale-dissolving tendency. If the water's pH (actual) equals its pH(s), it is just saturated and the LSI is 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, heating water, or potable hot water.

The temperature component in the LSI calculation is considered appropriate for 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 and boilers where values tended almost always to be positive, yet indications of deposition of calcium carbonate were absent. Experience shows 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

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

where

$$\begin{aligned} \text{pH}(\text{s}) &= (9.3 + A + B) - (C + D) \\ A &= [\log(\text{TDS}) - 1] / 10 \\ B &= -13.12 - \log[\text{temp } ^\circ\text{C} + 273] + 34.55 \\ C &= \log[\text{Ca}^{2+}] - 0.4 \\ D &= \log[\text{alkalinity}] \end{aligned}$$

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

Ryznar Stability Index (RSI). This index is a more accurate 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 revised the LSI equation. With his formula, 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. RSI gives more accurate results than LSI in waters with a pH less than 7.8, but still gives an indication of scale formation at higher pH values. Regardless, the RSI was useful for acid feed water treatment programs, which operated at pH < 7.8.

The RSI is calculated as

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

where 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(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 **pH(eq)** is used. As with the RSI, a PSI value of 6 indicates a calcium-carbonate-balanced 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. Use of the PSI is most applicable when cooling-water pH is above 7.5.

The PSI is calculated as

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

where 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 and 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 steam boiler or evaporative cooling-water system by intentionally diluting system water from the system via blowdown (bleed-off). 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.
- Make 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 chemical program designed to control scale and deposit formations in the boiler or cooling-water system.

Retention Time. 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 retention time** of system treatment chemicals, particularly biocides. 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 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 of the system, the higher the demand of scale inhibitor, 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 the system \approx evaporation rate (ER)/[cycles of concentration (CC) – 1]

Mechanisms. Water treatment chemical scale inhibitors work by the following mechanisms:

- **Threshold inhibition chemicals** control scale formation by dramatically extending the induction time required for deposit to form. If induction 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 to render scale nonadherent, fluid, transportable sludge instead of a hard deposit. Scale conditioners include lignin, tannins, and polymeric compounds.

Suspended Solids and Deposition Control

Strainers, filters, and separators may be used to reduce suspended solids to an acceptable level if required. A clean system is more efficient, with less corrosion, scaling, and fouling. Additionally, water treatment is also more effective in a clean system. Therefore, some systems can benefit from using the filtration methods described here.

Strainers. A strainer is a closed vessel with a cleanable screen designed to be removed for cleaning and to retain foreign particles down to 0.025 μm diameter from fluids. Screens with smaller than 0.025 mm (500 mesh) usually create excessive pressure drop for inline pumping. Often, a finer-mesh strainer is used to "clean up" a system after construction and then is replaced with a larger-mesh strainer to reduce pressure drop and the need to clean the strainer as often.

Strainers extract material to protect equipment downstream from constrictions or damage, and to allow saving the extracted product if it is valuable. Strainers are available as manual or automatic cleaning units, and may be made of cast iron, bronze, stainless steel, copper-nickel alloys, or plastic. Supplemental 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 0.102 to 0.00102 mm or smaller. Cartridge filters are typically disposable (i.e., once plugged, they must be replaced). The frequency of replacement, and thus the economic 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 for systems where contamination levels are less than 0.01% by mass (<100 mg/L). They are available in many different materials and configurations. Filter media materials include yarns, felts, papers, nonwoven materials, resin-bonded fabric, woven wire cloths, sintered metal, and ceramic structures. The standard configuration is a cylinder with an overall length of approximately 254 mm, an outside diameter of approximately 63.5 to 69.85 mm, and an inside diameter of about 25.4 to 38.1 mm, where the filtered fluid collects in the perforated internal core. Overall lengths from 101.6 to 1016 mm are readily available.

Cartridges made of yarns, resin-bonded, or melt-blown fibers normally have a structure that increases in density near 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. Beta ratios are used to indicate the ratio of particles entering the filter versus those leaving the filter. A high beta ratio means a more efficient filter.

Bag-Type Filters. 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 tubular pressure vessel with a hinged or clamped cover on top for access to the bag and basket. The inlet can be in the cover, in the side (above the bag), or in the bottom. 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).

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 <0.00102 to 0.838 mm. Felted materials are most common 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. 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 at the specified removal efficiency. 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, which conserves water. Multimedia vessels might also be used for low-suspended-solids applications, where chemical additives may be required.

Sand filters for cooling-water systems are usually high rate ($13.58 \text{ L}/[\text{s} \cdot \text{m}^2]$), with filter media rated from 0.00051 to 0.0102 mm. Some filter vessels are configured to allow water to enter at an angle to create a vortex-shaped filter bed and enhance removal efficiency. Total filtration rate is determined by either system volume turnovers or percent of circulation flow rate. Filter vessels are usually installed sidestream with a booster pump.

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 enter the unit tangentially, which sets up a circular cyclone flow path. The liquids are accelerated into the separation chamber. Centrifugal forces toss particles denser than the liquid to the side walls of the separation chamber. Solids drop along the perimeter and into the quiescent collection chamber. 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 a manual or automatic timed purge, or continuously bled from the separator bottom outlet 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. Disadvantages are that they do not remove particles with lower density than the primary liquid (e.g., cottonwood seeds) or fine particles $<40 \mu\text{m}$, and require periodic mechanical cleaning/service of the collection chamber.

The Handbook Online version of this chapter features separator animations.

General Notes: In specifying filtration systems, third-party testing by an accredited or independent agency should be specified. 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. When they are installed next to cooling towers, filter piping is used to sweep tower basin floors clean at a rate of 0.68 to $1 \text{ L}/(\text{s} \cdot \text{m}^2)$ via sweep ejector nozzles that can draw sediments behind the nozzles. This usually calls for a bigger booster pump to create the sweeping action. For this type of service, consultation with the filtration equipment manufacturer is essential to ensure proper application.

2.2 CORROSION AND CORROSION CONTROL

Corrosion is the destruction of a material, usually a metal or alloy, but it can include nonmetals like plastics, concrete, lumber, etc. The destruction process can be through chemical or electrochemical reaction with its environment. Common examples of those that can react are magnesium, aluminum, zinc, chromium, iron, tin-nickel, and lead. Examples of pure metals that are less reactive include copper, silver, platinum, and gold. Exceptions exist depending on the character of metal oxide surface films. Very tenacious surface oxide films can block corrosion of metals such as aluminum, chromium, nickel, and stainless steels. Corrosion is therefore a two-step process: (1) setting up reactive sites (anodes and cathodes) on contact surfaces and (2) establishing a continuing reaction between water and metal.

Depolarization involves a chemical reaction that fully or partially removes or weakens protective surface oxide films, thereby exposing base metal. Acidic conditions tend to dissolve protective films and produce uniform metal loss. High chloride tends to weaken protective film on metals so that subsequent corrosion is more irregular.

In most instances, the second 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 from the anode and often the formation of a deposit at the cathode. The rate of corrosion depends on the rate of flow of the electrons. Mechanisms for various types of corrosion are shown in [Figure 1](#).

Types of Corrosion

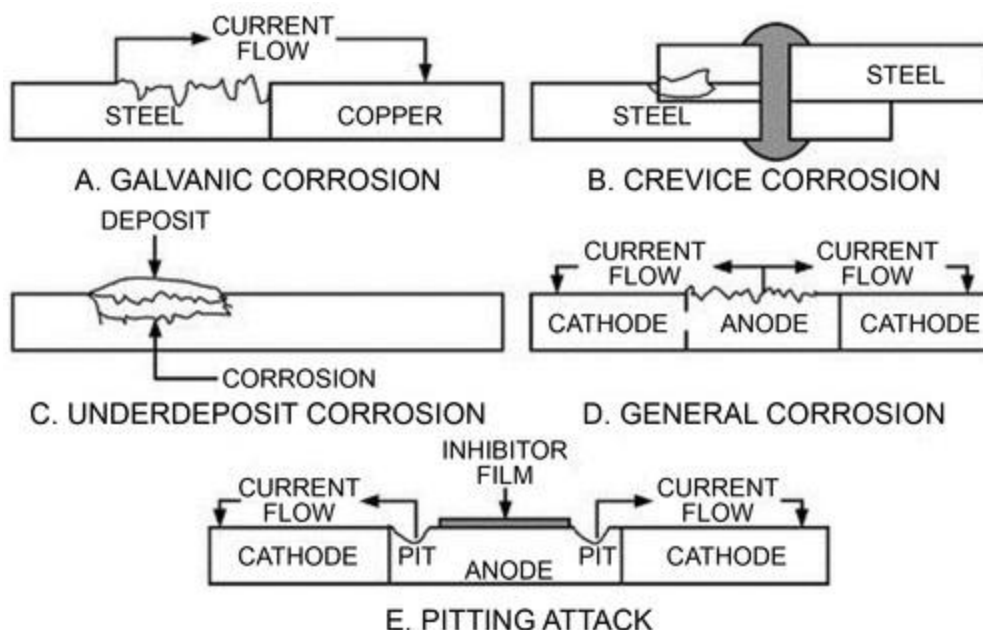


Figure 1. Corrosion Types and Mechanisms

Corrosion is often categorized into three broad categories: (1) readily identifiable through visual examination, (2) identifiable with supplementary means of examination, and (3) verifiable with microscopy. Group 1 covers the most prevalent types: general corrosion, localized corrosion, and galvanic corrosion for aqueous environments. Localized corrosion covers pitting, crevice corrosion, cracking, galvanic, and under-deposit corrosion. Many other types of corrosion associated with these three main categories are of concern in water treatment and encountered in boiler and cooling water systems for both HVAC and processes, including stress, fatigue, crevice, erosion, and microbiologically influenced corrosion. Corrosion in practical systems is rarely of one type but can be the result of an aggregate of several forms.

Uniform (general) corrosion ([Figure 1D](#)) is the most common type and is caused by a chemical or electrochemical reaction that results in the deterioration of the entire exposed surface of a metal. When general attack is due to chemical reactions, it is usually the result of either acid (low pH) or caustic (high pH) attacks. In near chemically neutral environments, general attacks are often initiated with differential oxygen concentrations, compounded with biofilms and deposits that create electrolytic anodes and cathodes on contact surfaces. General corrosion removes and weakens whatever protective metal oxide surface film may be present on a metal. Wetted metal surfaces below 66°C are often coated by biofilm. Beneath biofilm, pH is lower than in bulk phase water due to microbiological metabolism. This lower relative pH tends to weaken protective oxide surface films and expose subsurface elements to corrosive hydrogen ions.

Biological activity in and beneath biofilms also produces enzymes reactive with protective metal oxide surface films. Low pH and high chloride are primary contributors to the removal of protective iron oxide films from steel. Ultimately, 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 using corrosion-resistant construction materials, applying protective coatings, or providing appropriate cathodic corrosion protection. In some (but not all) cases, uniform corrosion can be controlled by changing the chemical environment. Raising pH and reducing chloride and total dissolved solids can reestablish protective surface oxide films on steel and ferrous alloys. The effects of uniform corrosion can be anticipated through measurement of material specimens exposed to the anticipated operating environment in a corrosion coupon rack. Metallic coupons are inserted in the rack for a predetermined exposure before being removed,

cleaned, weighed, and examined to determine rates of corrosion. Corrosion rates can also be measured with electrical probes and ultrasonic pipe wall thickness testers.

Localized (pitting) corrosion (Figure 1E) results from breakdown of surface protective oxides. Breakdown can be due to environmental factors, defective material, or inconsistent surface conditions. When a small defect or hole forms in protective metal oxide surface film, usually as the result of inconsistent inhibitor film formation at that location, this area becomes electrochemically 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 byproducts). Pitting is often the most serious form of corrosion, because the action is concentrated in a small area.

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 accelerated by the presence of oxygen and bacteria, which creates a localized adjacent cathode to the anodic surface of the pit, forcing concentrated anodic deterioration and enlarging the pit. See the section on Microbiologically Influenced Corrosion for more information.

Galvanic (dissimilar metal) corrosion (Figures 1A and 2) occurs when two different metals are located together in an 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. Galvanic corrosion is limited to the immediate area of the juncture of the two dissimilar metals. Deterioration of the anodic metal is most severe at the point of contact and diminishes markedly with distance. Galvanic corrosion rarely extends more than a few inches from where dissimilar metals make contact.

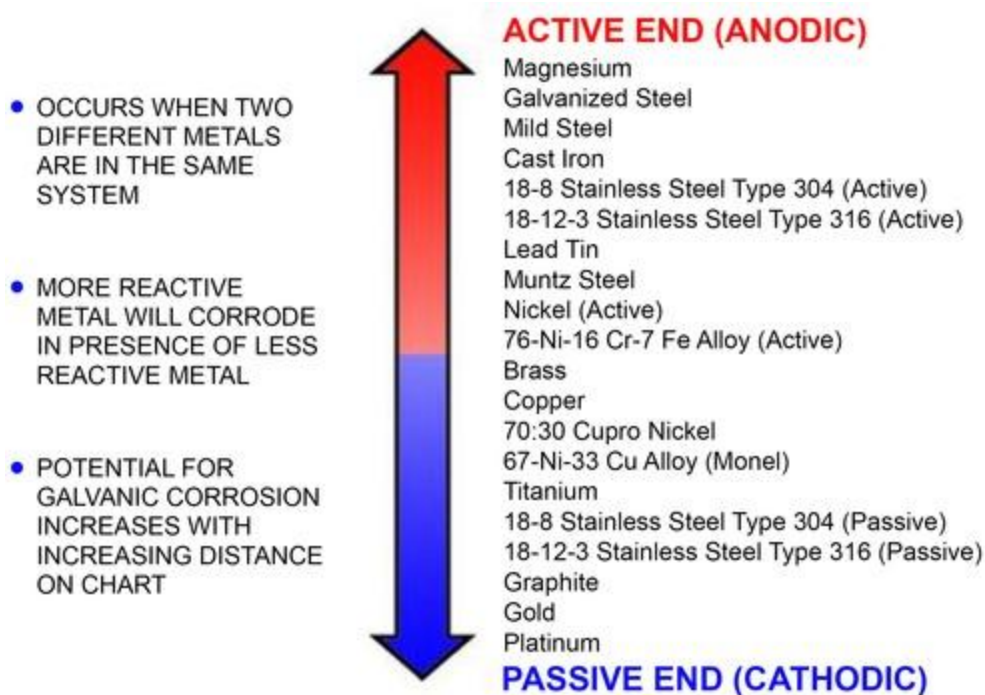


Figure 2. Galvanic Corrosion

Three conditions must exist for galvanic corrosion to occur:

- Electrochemically dissimilar metals must be present.
- The metals must be in intimate 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; galvanized (zinc) steel and steel or iron; and carbon steel and stainless 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 corrosive environmental conditions affecting the metal and in alloys subject to tensile stress. The stress may be applied, residual

(from processing), or a combination. The resulting crack formation can be transgranular or intergranular.

Corrosion fatigue is a result of combined action of cyclic stresses and a corrosive environment. Cyclic stresses (e.g., from rapid heating and cooling) are concentrated at points where surface defects exist, and corrosion has roughened or pitted the metal surface. Corrosive environments promote crack growth and reduce fatigue strength because of the action of applied cyclic stresses where a protective oxidation film fails on metal surfaces.

Caustic cracking occurs when metal is stressed in a fluid with a high caustic content, and a mechanism of concentration occurs at high water temperature in presence of silica. It is also known as **caustic embrittlement**. It occurs in boilers due to overfeeding, resulting in increasing caustic concentrations.

Crevice corrosion ([Figure 1B](#)) 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 is like concentration cell corrosion issues. As in pitting, the crevice allows the concentration of chlorides in the void and depletion of inhibitors and of oxygen, causing the crevice to become anodic and acidic to accelerate the reaction.

Erosion corrosion (flow-accelerated corrosion) occurs because 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, reduction of turbulence, and avoiding use of soft metals 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 to below its vapor point 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 caused or promoted by microorganisms, usually chemoautotrophs, which are microbes (usually bacteria) that can produce corrosive acids and enzymes as a part of their cellular metabolism. Bacteria do not attack metal or protective metal oxide surface films. Bacteria influence the chemical reactions between cathodic and anodic areas. The acids and enzymes cause attack, especially when bacteria create a biofilm. MIC can be a very serious problem in building HVAC recirculating water systems and wet sprinkler systems, involving many forms, mechanisms, and types of microbiological organisms, including the following.

- **Iron-related bacteria (IRB)**, such as *Gallionella ferrugine*, *Leptothrix ochracea*, *Cranothrix polysporer*, 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. These anaerobic organisms (i.e., they live without 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. Metabolic processes involve the transfer of electrons from a "food source" to an electron acceptor (oxidizing agent) for the purpose of obtaining energy and the building blocks for continued cell growth. The principal electron acceptor under aerobic (oxygen rich) conditions is oxygen. When oxygen is depleted or absent, SRBs can use sulfate as an alternative electron acceptor to oxygen. In the process, sulfate is converted to corrosive hydrogen sulfide.
- **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 into sulfuric acid, which is extremely corrosive and leads to localized under-deposit and pitting corrosion, often resulting in pinholes in system piping.
- **Biological deposits (BD; also called biofilms)** such as algae, yeast, molds, fungi, and bacterial slimes can also cause MIC. Even in the absence of specific corrosive organisms, biological deposits establish an environment for corrosion by establishment of concentration cells and lowering pH, resulting in under-deposit corrosion. Biological deposits also act as traps providing food for other organisms, accelerating metabolism and growth. This complex matrix sets up a corrosion potential between adjacent areas of a metal surface that may have different types of deposits. In general, the longer biological deposits are allowed to flourish, the more difficult, time consuming, and expensive they are to bring under control. They also create high resistance to flow (friction factor) and reduce heat transfer.

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. [Table 2](#) provide 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 humidity up to 99%. However, when contaminants such as sulfur dioxide or solid particles of charcoal are present, corrosion can proceed at relative humidity 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.

Table 2 Qualitative Classification of Corrosion Rates, mpy

Metal Classification	Low Carbon Steel	Copper Alloys	Galvanized Steel	Aluminum	Stainless Steel
Recirculating cooling water					
Excellent	<0.1	<0.1	<2.0	<0.5	<0.1
Good	1.0 to 3.0	0.0 to 0.2	2.0 to 4.0	0.5 to 2.0	
Fair	3.0 to 5.0	0.2 to 0.3	4.0 to 8.0	2.0 to 5.0	
Poor	5.0 to 10.0	0.3 to 0.5	8.0 to 10.0	5.0 to 10.0	
Unacceptable	>10.0	>0.5	>10.0	>10.0	>0.14
Closed cooling water					
Excellent	<0.2	<0.1			<0.1
Good	0.2 to 0.5	0.1 to 0.3			
Fair	0.5 to 1.0	0.3 to 0.5			
Poor	>1.0	>0.5			>0.1

Oxygen. Oxygen dissolved in water (DO) is a depolarizer at cathodes of corrosion cells, sets up differential aeration cells on metal surfaces, and feed aerobic bacteria to support MIC. However, it does not lead to continuous corrosion of active metals such as aluminum, chromium, nickel, and zinc because these metals form protective oxide surface films with dissolved oxygen acting as polarizing barriers that separate potentially oxygen-reactive metal from DO. Basic ferrous metals (steel and iron) form only porous oxide films susceptible to depolarization by numerous chemical and mechanical influences. Once depolarization of surface film on steel occurs, DO perpetuates the attack at anodes unless a protective film is formed and maintained by corrosion inhibitors (which reestablish film integrity). DO is needed for molybdate, a commonly used corrosion inhibitor, to work effectively.

pH. The pH of cooling water influences the potential of most metals to corrode. Corrosion tends to increase as pH levels decrease (become more acidic) because protective surface film tends to weaken or dissolve as pH falls below 7.0. However, different metals show different corrosion curves with respect to pH. Basic solutions are generally less corrosive to ferrous systems because they tend to make surface oxide film less soluble. It is practical in many water systems to minimize corrosion by adding caustic or alkaline buffering agents to raise and stabilize the pH between 9 and 11. Aluminum corrodes in both low pH (<4) and above a pH of 8.5 because its protective film weakens or dissolves outside this range; this reduces the acceptable range of pH in systems that contain both steel and aluminum.

Chlorides. Chloride is nonvolatile, commonly found in water, easily concentrated as water evaporates. Chloride ions can be adsorbed with the metals' protective surface film, weakening the film and making metal progressively more vulnerable to pitting and general corrosion, as chloride concentration rises and/or pH falls. Once protective film is depolarized, exposed elemental metal (generally ferrous and copper alloys) is free to react with oxygen. Because depolarization establishes an electrochemical circuit, the rate of reaction depends not only on the amount of oxygen present but also on the electrical conductance of the water; the higher the chloride and all other ionic species such as sulfate, sodium, potassium, etc., the more readily electrochemical activity proceeds.

Increasing the concentration of dissolved solids increases the conductivity of the electrolyte (water). Because a corrosion cell depends on the ability of the electrolyte to conduct the flow of electrons, the presence of more dissolved solids increases corrosion. For the corrosion reaction to proceed, a potential difference between anodic and cathodic areas is required. The potential difference between locations on a metal surface is caused by variations in solute concentration in the localized environment. The increase in corrosion caused by such conditions is called **concentration cell corrosion**. Crevices, cracks, pits, and foreign deposits on the metal surface can create conditions that contribute to corrosion due to differential dissolved oxygen levels. 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 based, available chlorides 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 replaced with corrosion-resistant material, isolated by an impervious coating, or properly inhibited.

Galvanic (Dissimilar Metal) Corrosion. Another factor that 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 relationship between anode and cathode:** 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. A larger anodic area relative to the cathode reduces the corrosion rate.
- **Intentional polarization of either cathodic or anodic areas:** technology is available to create polarization to reduce the potential difference between components of piping systems, large storage tanks, and various metal structures and thus reduce the rate of attack at points of naturally occurring anodic activity.
- **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 because the resistance to electron flow through water is reduced. Metal ions that are of higher galvanic potential than the contact metal may plate out on the contact metal surface and cause local galvanic corrosion.

Stress. Stresses in metallic structures rarely have significant effects on the uniform corrosion resistance of metals and alloys. Stress may be due to mechanical loading, vibration, large or cyclic temperature swings, repeated impact, or chemical or MIC gouging (acting alone or in combination). Stresses in some metals and alloys can cause corrosion cracking when the metals are exposed to specific corrosive environments. The cracking can have catastrophic effects. 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 and weaken protective surface films. Thus, corrosion rates are greatest in areas where temperatures are the hottest. Even temperature variations within a single piece of metal cause the warmer areas to become anodic to the cooler areas and corrode.

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 that depend on oxygen in the environment for maintaining a protective oxide film (e.g., stainless steel), 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. For example, zinc sacrificial anodes are ineffective in systems over 65.6°C.

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 impractical to control system corrosion by pressure control alone.

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

- Amount of oxygen in the water
- General chemical environment (e.g., low pH, high chlorides, high MIC potential due to sulfates)
- Temperature
- Suspended solids in the water
- Type of metal exposed (copper and iron are both susceptible)
- Flow rate

In metal systems where corrosion end products retard corrosion by acting as a physical barrier, high flow velocities may erode these protective barriers and increase the potential for corrosion. An excessively turbulent environment may cause uneven impingement attacks, from both erosion and corrosion. As mentioned earlier, this is called **erosion corrosion**. It is commonly found in piping with sharp bends and inlet ends of small openings 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 under-deposit corrosion, including concentration cell corrosion and microbial corrosion. Low flow velocity can also affect transport of corrosion inhibitors and polarization of corrosion cells.

Insoluble Solids (Turbidity) 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 increase erosion corrosion and biofouling. Under-deposit corrosion can form under 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 discussed in the microbiological and fouling control sections. They center on the contaminants and/or conditions that work to

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

Such conditions can be 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 (byproducts) as deposits. This highlights the importance of system maintenance and a good water treatment program to ensure system efficiency and longevity.

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. The specific choice of materials used in a system or piece of equipment must consider the expected operating conditions, potential upset conditions, expected system, lifetime, ease of replacement, and of course budget. The availability of many materials of construction options helps ensure that the proper choices can be made for a successful service life in most cases. When selecting construction materials, the following factors should be considered:

- Corrosion resistance of the material in the operating environment, including water quality.
- 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. 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 applied coatings must be used to prevent galvanic corrosion.
- Compatibility of chemical additives with materials in the system.
- Building codes and regulations.

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 depends on the surface preparation of the metal to be protected, coating thickness, and coating application technique. Coating durability depends on the adhesion between the coating and the metal. Adhesion depends greatly on surface preparation, including cleaning, degreasing, and the application of primers.

Defects in a coating are difficult to prevent. These defects can be 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 oxide lifting or cathodic disbondment. **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. Improved 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) results in an optimum condition between corrosion and scale formation.

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

- **Passivation:** these inhibitors form a thin protective oxide film on the metal surface, usually at anodic sites. Nitrites and molybdates work in this way.

- **Precipitation:** these inhibitors contain materials that are precipitated out of solution to form protective films at both cathodic and anodic sites in a corrosion cell. Silicates and phosphates work this way. They require oxygen for effective inhibition.
- **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 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 deviations 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 are molybdates, phosphates, zinc, phosphonates, silicates, nitrite-borates, aromatic azoles, and organics. Although very effective, chromate inhibitors are severely restricted because of their environmental toxicity and 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 anodic sites and reestablishing polarization. Though these inhibitors can be very effective, they can also be very dangerous if insufficient anodic inhibitor is present, because the entire corrosion potential can be focused at unprotected anode sites. Severe localized pitting attack can occur at unprotected anodic sites if insufficient inhibitor is present.

Cathodic corrosion inhibitors retard oxygen reduction at the cathode, form protective films at cathodes, and slow overall electrochemical activity. Cathodic inhibitors are not as effective as fully deployed anodic inhibitors, but are commonly used in conjunction with anodic inhibitors to reduce anodic inhibitor dosage requirement.

Combination corrosion inhibitors protect by forming a film on all metal surfaces, whether anodic or cathodic. Optimum corrosion inhibition is typically obtained through use of one or more anodic and/or cathodic inhibitor(s).

Adsorptive filming inhibitors are hydrophobic chemical additives that form a molecular film on metals to create a barrier to corrosion (analogous to paint but much thinner). A filming inhibitor bonds to metal through direct molecular charge interaction between the inhibitor and the metal's surface due to opposite electrical charge. Such bonding is quite strong. The class of copper corrosion inhibitors termed azoles is a good example.

Cathodic Protection. Sacrificial anodes reduce galvanic attack by providing a metal (such as zinc or magnesium) that is more active (anodic) in the galvanic series than two metals in a galvanic couple. A sacrificial anode becomes anodic to the surface metal and supplies electrons to relatively cathodic surfaces, thereby limiting the corrosion of the more anodic metal in the galvanic couple. Proper design and placement of anodes is important. When properly used, they can reduce loss of steel from the tube sheet and head cover of heat exchangers. 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 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, damage to metals by localized corrosion attack can be assessed through various means, such as eddy current testing of chiller tubes.

Corrosion Coupons. Using corrosion coupons is an accepted method for evaluating uniform corrosion rates in both closed- and open-loop systems. Coupon specimens can sometimes exhibit results of localized attack, most frequently from under-deposit and/or microbiologically influenced corrosion. Evidence of excessive localized attack on a coupon specimen may indicate invalid installation of the coupon specimen due to inadequate flow velocity and wrong position against the direction of flow. Careful selection, handling, placement, alignment, and recording of coupon specimens is required for accurate test results. Corrosion coupon racks are designed to comply with ASTM *Standard* D2688 to provide indication of adequate flow and direction of flow. Adequate flow rates and velocities of the fluid through the coupon rack are also essential to reflect system operating conditions: velocity of 1 m/s is normally used, and velocities in excess of 1.5 m/s may influence erosion, particularly of soft metals such as copper. Ideally, constant flow should be maintained throughout the test period and variable-flow piping systems should use pressure-independent flow control devices (automatic flow regulators) in the coupon rack piping. Coupon specimens should not be disturbed during a test.

Mild steel and copper are commonly used as coupons; admiralty grades of brass and various grades of stainless steel are less common. Regardless, coupon selection should reflect system metallurgy. Placement of the least noble coupon specimen should precede progressively more noble coupons in 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 to 90 days) yield more accurate results in operating systems than shorter tests (15 to 30 days). For new systems, first-30-days tests

can indicate the level of passivation during startup. 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, linear polarization resistance, electrical impedance microscopy, and acoustic wave emission probes. Linear polarization resistance and electrical resistance are common methods to 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 data-logged to assess trends in corrosion rates and system stability. Electronic sensors do 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.

2.3 BIOLOGICAL GROWTH CONTROL

Most heating equipment operates above normal biological temperature limits and therefore has fewer microbial problems. Hydronic systems operated below about 50°C provide conditions for growth and proliferation of microorganisms: abundant water, aeration, a possible supply of nutrients, and surfaces upon which to attach. Nutrients may include inorganic and organic compounds added directly to fight corrosion/scale/foam (e.g. nitrites, phosphate, phosphonate) or introduced as a process or operational contaminant. Problems associated with the uncontrolled growth of microorganisms in cooling or low-temperature heating water systems can be categorized in the following four areas:

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

Microbiological activity depends on, and reacts to, the specific conditions of a given water system. Clean, municipally treated, drinking (potable) water likely has extremely low biological activity. Wastewater and sewage are most likely highly biologically active. There are a vast number of different biological entities that can potentially be found in water, and the topic of microbiology is far too complex for involved discussion in this context, but there are a few key microbiological concepts that are very important to water treatment:

- All practical water systems have some degree of biological activity.
- Assimilable carbon is the primary component of biological activity, along with nitrogen and phosphorous.
- Biological activity appears in two forms: freely circulating organisms (planktonic) and organisms attached to surfaces (sessile); the same organism types may be found circulating or in biofilms.
- Sessile organisms form biofilm, which is present in all water conduits to a degree (even human arteries and the human digestive tract).
- Metabolism is an oxidation/reduction process involving transfer of electrons from an electron source (food/nutrient) to an electron acceptor, most commonly oxygen. Through this process, organisms obtain energy and the building blocks for growth and reproduction.
- Metabolism is fostered by biological catalysts (enzymes).
- Metabolism produces inorganic and organic waste products, which tend to be acidic/corrosive.
- Some organisms (aerobic) require oxygen to maintain metabolism and die or go dormant in the absence of oxygen (**obligate aerobes**).
- Some organisms (anaerobic) only use other electron acceptors (oxidizing agents), such as sulfate, and die or go dormant in the presence of oxygen (**obligate anaerobes**).
- Some organisms can metabolize with or without oxygen (**facultative anaerobes**).
- Chemical/biochemical conditions (e.g., pH, oxygen level, enzyme presence) may be considerably different under biofilm than in general water circulation (bulk phase water).
- Biofilm mass depends on nutrient availability, flow velocity, temperature, and oxygen.

- Small particles of biofilm, containing many microbes, freely detach from biofilm to migrate within a system and promote biofilm extension

Biological Categories

Microorganisms found in cooling-water systems generally fall into one of four categories: (1) bacteria, (2) algae, (3) fungi, or (4) macro higher forms. These organisms can enter a cooling system in various 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.

Bacteria. 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.” These are aerobic bacteria that thrive in an oxygenated environment. They are not harmful to the cooling system, because they do not directly cause deposits or corrosion, but they can provide nutrients for other microorganisms. Usually, the count of planktonic bacteria increases with increasing organic carbon nutrient as measured by the water’s chemical oxygen demand (COD) or its total organic carbon (TOC) content. In addition, some planktonic bacteria, such as *Legionella pneumophila*, are pathogenic and can present a significant human health risk.
- **Sessile bacteria** are non-swimming (attached) bacteria, sometimes called “stickers.” Sessile organisms cause most corrosion 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 are viscoelastic and can grow so large that they restrict water flow and interfere with heat transfer. They also may promote under-deposit 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 mesh 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. Sulfate-reducing bacteria (SRB), slime-forming bacteria (SFB), 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 assimilate 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 in 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 speciation's, and planktonic plate counts
- Online biofilm monitors, including corrosion-resistant coupons, disks/plugs, electrochemical sensors, fluorometry, 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. Corrosion may not be mediated by simply killing the planktonic microorganisms. Biofilm removal through chemical and/or mechanical cleaning is usually necessary. Corrosion 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.

Macro higher forms are bioincrustations colonized by large organisms. Macrofouling is common to once-through cooling systems due to buildups or infestations of Asiatic clams, zebra mussels or barnacles, bryozoans, and/or hydroids in marine environments at water intakes.

Control Measures

Eliminating sunlight from wetted surfaces such as distribution troughs, cooling media, and sumps significantly reduces algal growth. A distribution deck cover, which drastically reduces the sunlight reaching the algae in the water, 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 helps mitigate corrosion. Maintaining a high-quality disinfected makeup water supply with low turbidity and bacterial

counts reduces biological growth. Equipment should be designed with adequate access for inspection, sampling, and manual cleaning.

Mechanical aids include 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.

Usually, 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 products, and sediment in a cooling system also reduces the effectiveness of chemical biocides. Routine disinfection of cooling towers, including the use of high-level chlorination and a biodispersant, helps control *Legionella* as well as other microorganisms. Sidestream filtration and monitoring devices such as corrosion coupons, test spools, and biofilm sensors can enhance monitoring of biofilm growth. Alternating two different types of biocides can overcome resistance developed by bacteria against a single biocide. The two different types should include two different kill mechanisms.

More cooling-water treatment programs fail because of lack of microbiological monitoring and control than from any other treatment problem. Scale, corrosion, and fouling are often symptoms of poor microbiological control. Corrosion often occurs under bacterial slime layers. Inorganic foulants are trapped in slime layers, 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 an open cooling-water program to be successful.

An effective microbicide (biocide) program has five steps:

- Identify the types and concentrations of microorganisms present in the system.
- Select proper biocides based on system design, discharge restrictions, and types of microorganisms.
- Implement proper application, dosage, contact time, and control of the selected biocides.
- Perform seasonal disinfection cleanings.
- Understand system operation and piping layout to determine appropriate water sampling points to indicate worst system water conditions.

Microbicides. Chemical biocides used to control biological growth in cooling systems fall into two broad categories: oxidizing and nonoxidizing. There are numerous options commercially available. Some address a broad spectrum of organisms, whereas others are used to target specific types of organisms such as algae, SRBs, or fungi. Selection of the biocides should always be left to water treatment professionals.

Effective biocide treatment is usually a combination of an oxidizing biocide with a nonoxidizing biocide. The oxidizer may be fed continuously or intermittently. Nonoxidizing biocide may be introduced with either oxidizing biocide strategy. Oxidizing biocides provide quick-kill results and are best used to control biofilm; nonoxidizers are relatively slow acting and best used to suppress MIC activity. A biodispersant (surfactant) is often also incorporated to enhance biocide performance.

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. Chlorine dioxide is probably the one oxidizing biocide least affected by high chemical oxygen demand (COD) and total organic carbon (TOC). 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. 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 biocidal active (hypohalous acid) form. The residual oxidizing biocide concentration should be tested on a routine basis. Most halogenation programs can benefit from using dispersants or surfactants 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 are available, such as powders, pellets, or calcium hypochlorite sticks; chlorine-releasing compounds (e.g., chloramines, chloroisocyanurates). 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 it and because of environmental pressures concerning the formation of EPA-regulated halogenated disinfection by-products. In hot-water systems, including potable hot-water systems, chlorine loses efficacy up to 70% at temperatures 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 a gaseous form of oxygen consisting of three oxygen atoms (O_3). 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 decomposing organics destructing biofilms, and it requires significantly less chemical handling. The disadvantages of ozone are its short half-life, instability for storage (requiring on-site generation), and stringent EPA regulations on ozone reaction by-products. Use of ozone-generating equipment in an enclosed space requires safety protocols to protect operators from 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 time of the ozone with the circulating water. In larger systems, 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 gas is effective in low concentrations (0.2 to 0.8 mg/L residual). It must be generated on site. Unlike ozone, it is not affected by pH, and has a longer half-life and therefore a 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 as well as safety issues with precursor chemicals.

Hydrogen peroxide (H_2O_2) is a liquid that is usually available in concentrations of 35% or less, by mass, in water. Hydrogen peroxide is considered one of the most environmentally friendly oxidizing biocides, because it degrades to water. However, instability and the potential danger in handling concentrated hydrogen peroxide suppress its widespread use in high concentrations. It is usually used with a stabilizer to form peracetic acid.

Nonoxidizing Biocides. These 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.

When selecting a nonoxidizing biocide, many factors must be considered for its effective and efficient use, including system pH and relevant water chemistry, chemical compatibility with other treatment products and system contaminants, and the system turnover rate, or holding time index (HTI), for adequate microbial contact time. Common nonoxidizing biocides include the following:

- 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
- Aldehyde release treatments
- Organosulfur compounds

How 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 long enough 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 to overcome resistance developed by microbes.

Other Biocides. Ultraviolet (UV) irradiation deactivates microorganisms by cleaving DNA and nucleic acid molecules as the water passes around a quartz tube containing the UV lamp. The UVC spectrum covers the 200 to 280 nm wavelength, with most sources producing 254 nm light. The intensity of the light, thorough contact with the water, and adequate contact time are critical in obtaining a satisfactory kill of microorganisms. Suspended solids in the water or deposits on the quartz tubes significantly reduce the effectiveness of this treatment method. Therefore, a filter is often installed upstream of UV lamps to minimize these problems. Because UV light leaves no residual biocide in the water, sessile organisms and organisms that do not pass the light source are not affected by UV treatment. UV irradiation may be effective in humidifiers and air washers where the application of biocidal chemicals is unacceptable and where 100% of the recirculating water passes the lamp. It is less effective where all microorganisms cannot be exposed to the treatment, such as in cooling towers. Ultraviolet lamps require replacement after approximately every 9000 to 10,000 h of operation. The glass sleeves slowly accumulate deposits and become opaque to UV light, despite the use of wipers to keep the surface clean. UV lamp electrodes contain mercury, which requires special disposal for environmental protection. UV light can also be used to decompose chemical oxidants either to neutralize the residual oxidant or to promote advanced oxidation processes.

Copper (Cu) and silver (Ag) ions can effectively control microbial populations in water systems when the ionization systems that produce them are properly maintained, operated, and applied. Ions are released into the water via electrochemical means to generate 0.4 to 0.8 mg/L of copper and/or 40 to 80 µg/L of silver. The ions assist in the control of bacterial populations by interfering with electron transfer and denaturing protein by reacting with sulfhydryl, amino, and carboxylate groups. Copper, in particular, effectively controls algae. Cu and Ag treatment is not suitable for hard and alkaline waters. Prolonged treatment (over 3 years) can develop resistant strains.

Handling Biocides. All biocides must be handled with care to ensure personal safety. In the United States, cooling-water biocides 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 safety data sheets (SDS) and be provided with all appropriate safety equipment to handle each substance. An automatic feed system is preferred to minimize and eliminate handling of biocides by maintenance personnel. Several U.S. states (e.g., New York, New Jersey, Pennsylvania, Connecticut, Ohio, Rhode Island, Vermont, Indiana) require certified personnel to handle biocides.

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* serogroup 1 (Lp 1), one of the more than fifty known species of *Legionella*.

Legionellae are common warm-water, aerobic, gram-negative microorganisms that are mostly found in surface waters (lakes, ponds, rivers, streams) but can also be found in groundwater sources, including some soils. They tend to grow in biofilm or slime on the surfaces of lakes, rivers, and streams. *Legionellae* adapt to conditions in water distribution systems, thereby sometimes escaping municipal water plant disinfection (chlorination). 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 a risk for human disease.

The mere presence of *Legionella* does not necessarily result in disease. Several conditions and factors must occur: primarily, there must be enough and/or virulent forms 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 source. Aspiration of water can also occur during normal drinking and swallowing due to choking or gag reflex. Inhalation can bring 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, and is most probably influenced by host susceptibility.

Legionellae 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 to 41°C. The

subsequent use of water from such systems harboring *Legionella*, through faucets, shower sprays, humidifying, aerosolizing (misting) devices, or other spray or drift mechanisms of the system may transmit the 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 bicentennial convention in 1976. Since then, 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. The number of cases reported to the CDC has been on the rise since 2000. Health departments reported nearly 10,000 cases of Legionnaires' disease in the United States in 2018. However, because Legionnaires' disease is likely underdiagnosed, this number may underestimate the true incidence. A recent study estimated that the true number of Legionnaires' disease cases may be 1.8 to 2.7 times higher than what is reported. More illness is usually found in the summer and early fall, but it can happen any time of year. About 1 in 10 people who get sick from Legionnaires' disease will die.

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 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 *Standard* 188-2021 and ASHRAE *Guideline* 12-2020 for further information.

2.4 NONCHEMICAL AND PHYSICAL WATER TREATMENT METHODS

Nonchemical water treatment has been used for boiler water, cooling water, potable water, and other process applications for decades. There are multiple classifications of such treatment methods and equipment systems. 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. Water treatment technologies, published papers, and case histories should be evaluated considering water supply chemistry, operating environment, duty, and industry standard performance metrics.

Several 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 either 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 particulates, and force precipitation on these surfaces in the bulk water.

Cavitation systems can cause 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. The dispersion created by the device's electric field also inhibits biological growth.

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

Ultrasonic systems impart ultrasonic acoustic energy to a stream of water. The sound wave produced by ultrasonic devices can cause mechanical damage to bacteria cell walls. Like cavitation devices, ultrasonic energy can also produce low-pressure bubbles, which can collapse and damage bacterial cell walls.

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

Ozone systems inject 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

ASHRAE research projects RP-765 (Nasrazadani and Chao 1996) and RP-747 (Gan et al. 1996) found ozone only marginally effective in scale and corrosion inhibition, respectively. Ozone has been shown to have a very limited and unpredictable effect on calcium carbonate scale, and 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 or sessile microbial concentrations was observed in the (test) pilot-scale cooling tower for any of the devices, as compared to an untreated control tower.

Copies of ASHRAE research project final reports can be obtained from technologyportal.ashrae.org, and are free to ASHRAE members.

3. BOILER WATER SYSTEMS

Steam and hot-water systems can be classified into three broad groups: (1) steam and hot water for space comfort heating and humidity control; (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, physical configuration, heat source, and circulation. A general understanding of boiler design and classifications, as well as the 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 section is on steam and hot-water boiler systems for space comfort heating and humidity control.

Hot-water heating and low-pressure (103 kPa or less) steam systems with >95% condensate return are like 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 electric elements, or by direct firing in a heating-water boiler.

Steam generators range from small heating boilers to very large and complex systems generating steam for industrial plants and electric utility stations. All steam boilers operate on certain basic principles. Water is heated to produce steam at a desired pressure. The steam does work by heating a building or a commercial/industrial process. To conserve water, energy, and chemicals, the 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.

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, depend 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, including pretreatment equipment
- Guarded or unguarded plant certification status
- Training and qualifications of personnel
- Preventive maintenance program

- Control instrumentation and remote monitoring

The three most significant factors in setting up an economically viable and effective boiler water treatment program are the chemical properties of the makeup water supply, the rated steam output (kg/s), and the expected condensate return ratio.

Open Systems

Systems classified as open are routinely or continuously in contact with the atmosphere. Examples include steam systems that expose steam to confined spaces, such as autoclaves, and steam that sprays the moisture in an air stream, such as humidifiers that breathe in and exhale air. Open systems are constantly exposed to oxygen (a major corrosive element) and local trace gases. These systems require significant effort and cost to establish and maintain desired conditions.

Steam Systems

Scale in boilers is a direct result of precipitation of slightly soluble minerals (calcium, magnesium, iron, and silica) from the boiler feedwater. Scale can be prevented by removing a portion of the scale-forming ingredients prior to the boiler with external equipment, or within the boiler water 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 phosphate/carbonate. These sticky, adherent sludge deposits are caused by excessive amounts of iron entering the boiler with the feedwater. This iron is in the form of iron oxide and/or iron carbonate corrosion products. It is a result of corrosion taking place in pre- and post-boiler sections, 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.

3.1 EXTERNAL BOILER WATER PRETREATMENT (WATER CONDITIONING)

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 chemical additives and conditioners as consumables. Selection criteria should include the effects of all components, as well as local water type and sanitary discharge regulations.

The most common sources of corrosion in boiler systems are dissolved gases: oxygen, carbon dioxide, and ammonia. Of these, oxygen is the most aggressive, potentially leading to pitting of boiler tubes. 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.

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 the dissolved oxygen. Although deaerators can reduce dissolved oxygen to about 7 µg/L, trace amounts are still present and can cause corrosion. 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 common oxygen scavenger is catalyzed sodium sulfite. It is very effective and can be easily measured in the water.

In smaller steam boilers, mixing of makeup water and condensate normally occurs in an unpressurized, vented 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.

Types of pretreatment for boilers include the following:

- **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 a less 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 appropriate ions. Ion exchange resins can be classified in two groups: anion exchanger and cation exchanger.
 - **Sodium 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 media used to be sodium zeolite mineral, but is now replaced with the synthetic resins polystyrene and divinyl benzene. 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 a 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). A 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 through individual anion and cation exchanger vessels in series. Deionization removes virtually all anions and cations in the incoming water, replacing them with H⁺ and OH⁻, which in turn form water. Deionizers are often regenerated off site by a third-party service, although large systems (microchip manufacturers) may have automatic regeneration with acid and caustic soda, which requires 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** allows water to pass through a semipermeable membrane while preventing most dissolved minerals 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 total pretreatment system water input by 20 to 50% because of the increased water requirement of the concentrate stream, although it may be possible to reuse this stream for other applications on site.
- **Reverse osmosis (RO)** produces the highest quality (lowest dissolved mineral content) of all membrane separation technologies. Typical removal rates are >95%. 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.
- **Mechanical deaeration (deaerators)** (1) remove oxygen, carbon dioxide, and other non-condensable gases from steam 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 to remove dissolved gases, primarily oxygen.

Boiler Feedwater

After pretreatment to remove hardness and other problem impurities, the makeup water is combined with returned condensate to become boiler feedwater. In larger boilers, the mixing of makeup water and condensate normally takes place in the deaerator.

Makeup water introduces appreciable amounts of oxygen into the system. Oxygen can also enter the feedwater system via 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, heat exchanger air vents, and leakage of non-deaerated water used for condensate pump seal and/or quench water. Using vacuum pumps to return steam condensate can remove air from the return piping and enable faster condensate return to boiler feed water tank.

Boiler Internal Treatments

Even after the best 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 potential problems and 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/or precipitation programs. Chelates, polymers, and acrylates work by binding the hardness, thereby preventing precipitation and scale formation. Phosphates and carbonate programs work in combination with sludge conditioners (tannins, lignin, starches, and synthetic polymers) to produce a softened precipitate that is removed by blowdown of the steam boiler.

Prevention of Corrosion and Oxygen Pitting. Although steam 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 also to the steam and condensate systems. 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. Corrosion inhibitors are also used as regular treatment for low-pressure steam (<15 psi) boilers where oxygen scavengers alone cannot control corrosion completely.

Steam Boiler Lay-Up. Most of the corrosion damage to boilers and associated equipment occurs during idle periods. This 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.

Although sulfite introduction to remove oxygen is the most common form of treatment for steam boilers, it is not always the most effective for various operational reasons that prevent adequate maintenance of the required continuous sulfite residual. Sulfite maintenance can be particularly difficult in low-pressure heating boilers, most often operated without feedwater deaeration. To deal with this situation, boiler corrosion-inhibitor treatment strategies have been developed that do not primarily remove dissolved oxygen, but act to restore a stable protective oxide surface film on steel. Various chemicals such as nitrite, molybdate, erythorbate, diethyl-hydroxylamine and others act to prevent oxygen attack by creating a stable oxide film on steel.

Wet Boiler Lay-Up (Steam Boiler). 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. 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. 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). As more steam is produced and feedwater is introduced, the concentration of these dissolved and suspended solids increases (and with it, sludge formation). The increased alkalinity and dissolved minerals decrease boiler water surface tension. This leads to the formation of water droplets that can carry over with the steam, causing wet steam. Wet steam can cause water hammer, erosion corrosion of the steam network, and increased condensate drainage from drip traps. Implementing blowdown can decrease the concentration of dissolved and suspended solids. There are two types of boiler blowdown: continuous (or surface) blowdown and manual (or bottom) blowdown.

Continuous (or surface) 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 not included on all boilers. 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, foam, and floating impurities. The manual graduated valve can be automated with a motorized ball valve, a flow regulator, a high-temperature conductivity probe, and a controller to blow down based on conductivity limit set points.

By code (ASME 2015), all steam boilers must include a means for **manual (bottom) blowdown**. Manual blowdown allows removal of solids that settle at the bottom (mud-drum or belly) of the boiler. Bottom blowdown is used to remove precipitated sludge from the boiler mud drum. 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, feedwater quality, type of chemical treatment program, and safety practice. 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.

Boiler Blowdown Guide. 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 losses. Contact the boiler manufacturer for the recommended blowdown procedures. If none are available, the following can be used as a general guide:

1. Open the quick-opening valve (ones closest to the boiler).
2. Open the slow-opening valve.

3. Blow down the boiler for the amount of time specified by the water treatment consultant by opening and closing the slow-opening valve. Pay close attention to the water level in the gage glass. Some loads require several short blowdown cycles to maintain the proper water level in the boiler.
4. Close the slow-opening valve.
5. Close the quick-opening valve(s).
6. Open the slow-opening valve again to drain the line between the quick- and slow-opening valves.
7. Close the slow-opening valve again and double-check that the shutoff is tight after the valve has cooled off.

Note: Never pump the quick-opening valve to blow down the boiler. Such action could cause water hammer and damage piping and valves. It could also cause personal injury. Never leave an open blowdown unattended. Remember the valve(s) closest to the boiler must be opened first. Manual blowdown should be done with the boiler under a light load when possible.

Controlling the continuous blowdown rate is important to prevent the problems associated with high levels of 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

Other problems associated with steam and condensate systems include general corrosion and pitting corrosion. Naturally occurring bicarbonate alkalinity in the boiler water breaks down to form carbonate ions and carbon dioxide (CO₂). CO₂ leaves the boiler with the steam. As the steam condenses and becomes condensate, it dissolves some of the CO₂ to form carbonic acid, lowering the condensate pH. To prevent condensate corrosion, these systems must be protected from acidic conditions and oxygen, which lead to general and pitting corrosion respectively. Protection can be mechanical (deaeration/dealkalization), chemical, or include both means. The following methods are commonly used for condensate system protection.

Protection from General Corrosion.

Mechanical. Reduce alkalinity from boiler feedwater to minimize the amount of CO₂ in the system. As discussed in the boiler water pretreatment section, alkalinity can be reduced by dealkalization, demineralization, and reverse osmosis. In many cases, mechanical reduction of alkalinity is not needed because of low-alkalinity makeup water and/or feedwater.

Chemical. 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 common 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 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 have different basicity, neutralizing capacity, and distribution ratios. 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. Reduce oxygen from all steam boiler feedwater to prevent oxygen carryover to the steam and condensate system (via mechanical methods and chemical oxygen scavengers).

Chemical. One method includes feeding 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. Carryover in low-pressure boilers and high pH can reduce the effectiveness of filming amines. Filming amines can form and move old deposits in old piping. Combining neutralizing and filming amines is a successful alternative to protect against both acid and oxygen attack.

Another practice is to feed a volatile oxygen scavenger to the steam. 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 mechanisms should be considered. Proper injection points for treatment

chemicals are important in attaining optimal results from the water treatment programs. Handling, delivery, and disposal of containers must be considered. Onsite 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.

4. OPEN COOLING WATER SYSTEMS

Cooling Tower Treatment. The following guidelines are based on ASHRAE *Guideline* 12-2020 for start-up (or recommissioning) and shutdown for offline cleaning and disinfection of cooling tower systems. Local laws and regulations may supersede the guideline's practice.

Start-Up and Recommissioning for Drained Systems

1. Inspect tower interior for airborne debris and storm or weather related damages. Determine the extent of cleaning and repairs needed.
2. Isolate tower basin discharge with a temporary cover.
3. Clean all debris, such as leaves and dirt, from the cooling tower. Remove the temporary cover.
4. Close building air intakes around the cooling tower to prevent entrainment of biocide and biological aerosols in the building's air-handling system.
5. Fill the system with water. While operating the condenser water pump(s) and *before operating the cooling tower fans*, execute one of the following two biocidal pretreatment programs:
 - Add low-foam detergent and defoamer per water treatment consultant's recommendation.
 - Resume treatment with the oxidizing 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).
 - Treat the system with sodium hypochlorite or bromine at a level of 10 mg/kg free halogen residual at a pH of <8.0 with chlorine or <8.5 with bromine. The residual level of free chlorine should be held at 4 to 5 mg/kg for 5 h.
6. Drain system piping for cleaning of piping components and removal of biofilms and debris, following all applicable rules and regulations and obtaining all permits that may be required.
7. Refill system and add oxidizer to impart at least 10 mg/kg of free halogen for an hour.
8. Turn off circulating pumps and drain system piping.
9. Refill the system. Return all chemical feed and control equipment to normal operation, consider re-passivation of system metallurgies, and resume water treatment.

Start-Up and Recommissioning for Undrained (Stagnant) Systems

When water remains stagnant for more than about 24 h, dissolved oxygen may deplete, and microbiological conditions may change unfavorably. The environment may become increasingly favorable to MIC activity, as well as *Legionella* growth. The likelihood of this occurring increases if sulfates and COD are high, or if significant amounts of silt or sludge are present. It is always best to clean a cooling tower system at the end of a cooling season rather than waiting until the start of a new season.

To avoid issues with undrained systems, recirculate the system water periodically (every 24 to 48 h) to turn over the system volume several times and to add water treatment chemicals as well as keep the chemicals mixed. Systems that have been idle for 5 days or more should implement the following procedure:

1. Inspect tower interior for airborne debris and storm or weather related damage, and determine the extent of cleaning and repairs needed.
2. Remove accessible solid debris from bulk water storage vessel (cooling tower sump, drop tank, etc.).
3. Close building air intakes around the cooling tower to prevent entrainment of biocide and biological aerosols in the building's air-handling system.

4. Leave tower fans off. Perform pretreatment procedures (described in the section on Start-Up and Recommissioning for Drained Systems) directly to the bulk water storage vessel.
5. Avoid circulating stagnant bulk cooling water over cooling tower fill or operating cooling tower fans during pretreatment.
6. Stagnant cooling water may be circulated with condenser water pumps if tower fill is bypassed. Otherwise, add approved biocide directly to the bulk water and mix with manual or sidestream flow methods to evenly distribute the dosage. Take care to prevent creating aerosol spray from the stagnant cooling water from any point in the cooling-water system.
7. 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 (typically >5 days), the entire system (cooling tower, system piping, heat exchangers, etc.) should be chemically treated per ASHRAE *Guideline* 12-2020.

Standby (wet). Whenever the system is shut down or out of service, or when portions of the system are nonoperational for less than 5 days, without draining the water, take the following steps:

1. Maintain the system's water treatment program (microbial, corrosion, and scale/sediment control) along with normal monitoring practices. When an automated biocide program is in use, adjustments to the feed program may be necessary to ensure the biocide is added while the system is circulating and not skipped once the system is in standby.
2. Circulate water at least three times a week throughout the open loop of the closed-circuit cooling tower and the entire open circuit cooling system, including any basin sweeping and filtration systems. This periodic circulation will help restore control of water treatment parameters and help control biological growth.

Shutdown (dry). Whenever the system is expected to be shut down for an extended period, the system should be drained and put into a dry, offline position. A dry shutdown is often implemented when the system is not needed for an extended period due to seasonal conditions, such as cold winter temperatures. The following actions should be taken for a dry shutdown:

1. Drain and properly dispose of all system water, including water in the cooling tower, system piping, heat exchangers, and filtration systems. Open appropriate valves so that the entire system and all dead legs drain. If possible, the system should be air blown to force water out of low spots in the lines. It is recommended to keep the system closed until it is needed again.
2. Periodically inspect the open-circuit cooling tower, closed-circuit cooling tower, or evaporative condenser and clean any debris such as leaves and dirt from horizontal collection surfaces of the exposed equipment.

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 (ZnCO_3).

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 mg/L (3 grains as CaCO_3), requiring the evaluation of the use of water softeners on makeup water during passivation.

Contemporary cooling tower treatment programs generally involve the addition of phosphate-polymer-based scale and corrosion inhibitors and operating cooling-water systems at pH above 7. Water chemistry at high pH levels (8 to 10) 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 mg/L hardness (as CaCO_3) can also be corrosive to galvanized steel. This applies to natural soft makeup water at locations where water supplies are from snow melt and surface rainwater.

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 should include moderate hardness levels of 100 to 300 mg/L as CaCO_3 and alkalinity levels of 100 to 300 mg/L as CaCO_3 and chloride <125 as Cl^- to promote passivation. Where pH control is not possible or practical (e.g., makeup water is >8 pH), phosphate-based inhibitors may help protect galvanized steel. Many cooling tower manufacturers adopt the above approach as part of their warranty conditions for protection of galvanized cooling towers. Using 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.

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. Cathodic protection with sacrificial anodes is often incorporated to protect heat exchangers.

Open Recirculating Cooling-Water Systems

In an open recirculating system, chemical use will be higher because the water composition changes significantly by evaporation, thus concentrating the corrosive and scaling constituents. However, most chemicals are also concentrated 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

- Control of scaling indices and cycles of concentration using a conductivity controller
- Alkalinity control using automatic injection of sulfuric acid based on pH
- Scale control with polymeric dispersant, administered using contacting water meters, proportional feed, or traced control technology
- Oxidizing biocide control using an ORP (oxidation-reduction potential) controller and online monitoring of oxidant levels
- Nonoxidizing biocide control using timers, proportional feed, or traced control technology

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 enough (by evaporation) 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 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.

5. CLOSED SYSTEMS

Common Elements. All closed loops need a mechanism to introduce chemicals into the system. Pot feeders are the most common tool used for small to medium sized systems, but chemical pumps can also be used to introduce the chemicals.

- **Water meters:** Each closed-loop system should be outfitted with a makeup water meter to measure the amount of water fed into the system. A log of the readings should be kept to help detect leaks and track water usage.
- **Corrosion coupon racks:** Closed loops should be outfitted with a two- to four-position corrosion coupon rack with a flow meter/flow regulator to verify that the flow rate through the rack is appropriate and representative of the system (generally 0.9 to 1.5 m/s).
- **Filter feeders:** 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 and allows the unit to become a filter once a filter bag or cartridge is added. Filtration can occur down to submicron ($<0.5\ \mu\text{m}$) levels. When filtration is needed, the easiest solution for smaller systems is replacing the pot feeder with a filter feeder. Filtration down to $5\ \mu\text{m}$ size is desirable; however, dirty systems should start with $>25\ \mu\text{m}$ size filtration to allow cheaper coarse filters to do their work first. The optimum size can be determined by a particle size distribution analysis.
- **Filtration:** New pipe has varying degrees of moderately loose iron oxide based mill scale. Over time, and with repeated expansion and contraction due to temperature change, mill scale is eroded and adds small particles of highly abrasive debris to flowing water. This material can cause roughening of valve seats, scoring of valve stems, and abrasive damage to packings and mechanical seals. Pretreatment cleaning often leaves turbidity and suspended solids behind due to the presence of hideout areas and inadequate makeup to allow thorough flushing. Properly sized sidestream filtration is recommended to reduce possible abrasion of working surfaces in closed-loop systems. Ideally, stainless steel bag filter housings are used to provide wider selections of filter bags, flow rates, and housing configurations.
- **Filter installation:** Pressure differential 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. Filter housings should be equipped with isolation valves, unions, vents, and drain valves to facilitate service. Modern heat exchange design includes mechanical advantages such as finned tubes, internal rifling, compact brazed plates, and increased surface area, and are prone to fouling. Increased filtration minimizes the fouling and increases system efficiency.

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. Modern heat exchange design includes mechanical advantages (e.g., finned tubes, internal rifling, increased surface area) that are prone to fouling. Increased filtration minimizes the fouling and increases system efficiency.

Closed Recirculating Systems (Closed Hydronic Loops). Common examples of these include heating-water, chilled-water, combined cooling and heating, and closed-loop condenser water systems. The most common distinction defining a closed system is that the method of cooling is not evaporative. Minimal water loss/makeup and minimal air contact are two additional conditions typically associated with closed loops.

In a closed recirculating system, water composition remains 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 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 biofilms 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. One of the most problematic challenges for closed-loop systems is contamination from glycol-based antifreeze used to "winterize" air handler coils. Although the amount of antifreeze contamination amounts to just a few hundred milligrams per litre or ppm of system volume, breakdown of glycols can produce enough acidic byproducts to lower pH throughout the recirculating water and establish system-wide corrosive conditions.

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 and abrasion damage is done to new systems because of improper start-up procedures. In many cases, filling a system with untreated water for the purpose of performing pressure tests causes this problem. Typically, the system is then left stagnant, sometimes for many months, until it is ready to be commissioned. During that time, anoxic conditions persist, promoting MIC and under-deposit corrosion. MIC will waste system metals, sometimes considerably.

New systems should never be filled with untreated water and should not be left stagnant for long periods of time, even when treated. New systems should be thoroughly cleaned and flushed with an appropriate pretreatment chemistry as early as possible, preferably with the initial filling.

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, reviewed at least annually. Yellow metal corrosion inhibitors are included in most systems. Mixed-metallurgy corrosion inhibitors should contain appropriately dedicated corrosion inhibitors for the metal composition of the system.

The chemical manufacturer's recommendations should be followed regarding inhibitor concentrations maintained in the system.

HVAC Closed Loops Containing Aluminum. 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 and require controlling pH more narrowly than other systems. The increasing popularity of aluminum boilers has made this a much more common issue.

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 pH environments. Manufacturer specifications should be followed (generally not to exceed 8.5 pH).
- Free copper should generally be maintained <0.1 mg/L with a copper inhibitor.
- Total aerobic bacteria counts should be controlled to less than 1000 colony-forming units per millilitre (cfu/mL).
- Turbidity should be <10 FTU/NTU.
- Filter media sidestream should be <0.5 µm.

Thermal Storage Systems

Thermal storage systems require the same attention as other systems for 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, particularly in storage tanks. The system should be equipped with a filter to facilitate solid removal. Either a physical or instrumental method of corrosion monitoring should also be used to ensure that acceptable corrosion rates are maintained.

Perhaps most important regarding large chilled-water thermal storage (CWTS) systems is having a clear understanding of the treatments recommended. Because water and water treatment additives remain in a CWTS system for many years, the eventual fate of all additive components should be clearly detailed and understood prior to addition. Proposed organic compounds should receive special consideration by virtue of their potential biological nutrient value (i.e., biochemical oxygen demand [BOD]).

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 38 to 93°C, require sufficient inhibitors to control corrosion. For more information on treatment selection for these systems, see the section on Corrosion and Corrosion Control.

Medium and High Temperature. Medium-temperature water-heating systems (121 to 177°C) and high-temperature, high-pressure hot-water systems (above 177°C) require careful consideration of treatment for corrosion and deposit control. Makeup water for such systems should be demineralized or softened to minimize scale deposits and deaerated. 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 manufacturer’s specifications. 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. Other high/medium-temperature hot-water generators may have expansion recirculating tanks that require steam-phase treatment. Volatile oxygen scavengers that can passivate are usually used. Heat exchange at terminal units may use copper heat exchangers, in which case copper inhibitor should be incorporated.

5.1 ANTIFREEZE SYSTEMS

Glycol Systems

Glycol systems are closed-loop water systems that usually contain over 20% (by volume) of either propylene glycol or ethylene glycol (aka antifreeze). Premixed aqueous glycol solutions are typically available from vendors. There are three common types: (1) ethylene glycol (toxic), (2) propylene (nontoxic), and (3) food-grade propylene glycol (nontoxic and government certified). All glycols have a sweet taste, which makes spills of ethylene glycol a health concern. Where toxicity is a concern, HVAC applications use propylene glycol, although its pumping and heat transfer properties are inferior to those of ethylene glycol. Glycol is commonly used as a coolant in closed evaporative cooler circuits, and in chilled- and hot-water circuits that are exposed to freezing temperatures.

Table 3 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
–18.0	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

In geothermal cooling and heating systems, if not using food-grade propylene glycol, sometimes a mixture of water and alcohol is used, typically ethanol rather than methanol or propanol because ethanol is safer than methanol and has lower freeze point and viscosity than propanol.

To protect against freezing during seasonal lay-ups, glycol may be added 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 25 to 50% glycol in fall (before seasonal shutdown) to prevent freezing. They are then drained and flushed before summer start-up to resume normal operation. Inhibited glycol, when diluted to below 20%, loses its biocidal 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 and using automatic glycol tank makeup systems that contain premixed glycol to prevent dilution by domestic water makeup. Flushing laid-up coils without testing for trace glycol can lead to trace glycol contamination, which can cause high turbidity, corrosiveness, and repulsive odor. See [Table 3](#) for data on glycol and freeze protection.

Treating antifreeze systems is like 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 to protect those metals. Phosphate-based detergent is also preferred over silicate-based detergent 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. City water makeup should be avoided. Its entry can dilute glycol and its inhibitor concentrations to an unstable level. Dilution below 20% can initiate biodegradation as well as oxidation (decomposition by dissolved oxygen). Hence, makeup only be fed by an automatic antifreeze (glycol) feeder. Use only industrial HVAC glycol-based heat transfer fluids. Do not use automotive antifreeze (glycol) because it contains different additives, has silicate-based inhibitors, and has different thermal properties. Do not change glycol products without verifying the corrosion inhibitors they use. Most glycols use a phosphate inhibitor, but at least one vendor uses nitrite. Makeup water should have total hardness <50 mg/L as CaCO_3 , chloride as Cl^- <25 mg/L, sulfate as SO_4 <25 mg/L, and turbidity <1 NTU to minimize phosphate precipitation and to protect against corrosion.

When inhibitor levels are out of balance, inhibitors may be fed with a bypass filter feeder to control pH, alkalinity, turbidity, and inhibitor levels. An inhibitor program protects multimetal materials, steel, cast iron, copper, brass, and solder with buffered pH between 8 and 9.5; 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. New glycol shall comply with ASTM *Standard* D1384 (less than 10 mg of metal loss in 2 weeks of all system metals).

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.

Ethanol Systems

Inhibited ethanol (ethyl alcohol) antifreeze is often specified for geothermal cooling systems. It is less viscous and has slightly better thermal conductance than propylene glycol. It is also less toxic than ethylene glycol and methanol. It is thus considered safer for the environment and acceptable for ground-source heat exchangers (also called borehole heat exchangers) in some states. However, it is flammable and has a low boiling point, making it a potential fire hazard and risky for storage and handling. Hence, it is not widely accepted as an alternative to propylene glycol and brine. Because it is prone to decomposition by oxidation, its inhibitors usually contain oxygen scavengers/reducing agents like sodium sulfite with pH buffering agents, polymeric dispersants, and ferrous and copper corrosion inhibitors. Common applications involve an aqueous mixture of 20 to 25% of inhibited ethanol with slightly alkaline pH (8.5 to 9.5). It also requires soft makeup water with low mineral content, such as chloride and sulfate, and adequate reserve alkalinity.

6. TERMINOLOGY

The following terms are commonly used in the water treatment industry. Additional terms are defined in the section on Water Characteristics.

Alkalinity. The sum of acid-neutralizing anions: bicarbonate, carbonate, and hydroxide ions in water. Other ions, such as borate, phosphate, or silicate, also contribute to alkalinity. Alkalinity is expressed as mg/L of CaCO_3 . Reserve alkalinity (RA) is the number of millilitres, to the nearest 0.1 mL, of 0.100 N hydrochloric acid required for titration to a pH of 5.5 of a 10 mL sample of undiluted, unused antifreeze coolant.

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

Anode. The positive electrode of an electrolytic cell at which oxidation (loss of electrons) occurs.

Biological deposits. Water-formed deposits of biological organisms or the products of their life processes. Examples include barnacles, algae, and bacterial slime (biofilm). Biofilm formation can also be found in the arterial and digestive systems of animals and people.

Bleed off/blowdown. Water intentionally discharged from a system to limit buildup of dissolved and/or suspended solids.

Cathode. The negative electrode of an electrolytic cell at which reduction (gain of electrons) 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.

Cycles of concentration. Water vapor lost from a cooling tower, and steam or condensate lost from a boiler system, is free of dissolved solids and must quickly be replaced by makeup water to sustain system operation. The incoming water has dissolved solids; therefore, dissolved solids accumulate in system water. Cycles of concentration can be defined as the ratio of dissolved solids system water to dissolved solids in makeup water. More precisely stated, it is the ratio of the volume of makeup to the volume of bleed off/blowdown.

Electrolyte. A solution through which an electric current can flow. Water without ions present in it does 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 . It is divided into temporary hardness (from carbonate and bicarbonate) and permanent hardness (from strong non-carbonate anions like chlorides and sulfates).

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

Ion. A positive (cation) or negative (anion) electrically charged atom or group of atoms.

Makeup. Water added to a cooling tower or boiler system to replace evaporation or steam loss.

Passivity. The tendency of a metal to become inactive in its 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 [$-\log_{10} = \log(1/\text{H}^+)$]. pH values below 7 are increasingly acidic; those above 7 are increasingly alkaline. Each whole unit change in pH represents a 10-fold change in hydrogen ion concentration.

Polarization. The deviation from the open circuit potential of an electrode resulting from the passage of current. Also used to describe the reduction of electron flow where corrosion of an active metal is possible. Depolarization implies continued passage of electron flow and likely corrosion activity.

Potable. Safe to drink. In the U.S., this normally means water that complies with the *National Primary Drinking Water Regulations* (NPDWR; EPA 2009). The NPDWR document is also an excellent source of information about the adverse effects and sources of each regulated contaminant. Some states may also adopt the *National Secondary Drinking Water Regulations*, which are shown at the end of the NPDWR document and affect cosmetic issues and taste, but not health.

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 mixture of liquid and sedimentary water-formed deposits, originating from (1) organic materials and biological sources, (2) capture of suspended particles from the air, and/or (3) in-system-formed hardness or corrosion debris. *Note:* sludge deposits can harden over time, or upon drying, and take on the appearance of scale.

Tuberculation. The formation of tubercles (small mounds of corrosion products) over a metal.

Water-formed deposit. Any accumulation of insoluble material derived from water or formed by the reaction with water and oversaturated minerals on surfaces.

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