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Cleaner Water through Applied Chemistry & Biology

Water Treatment for Cooling Towers

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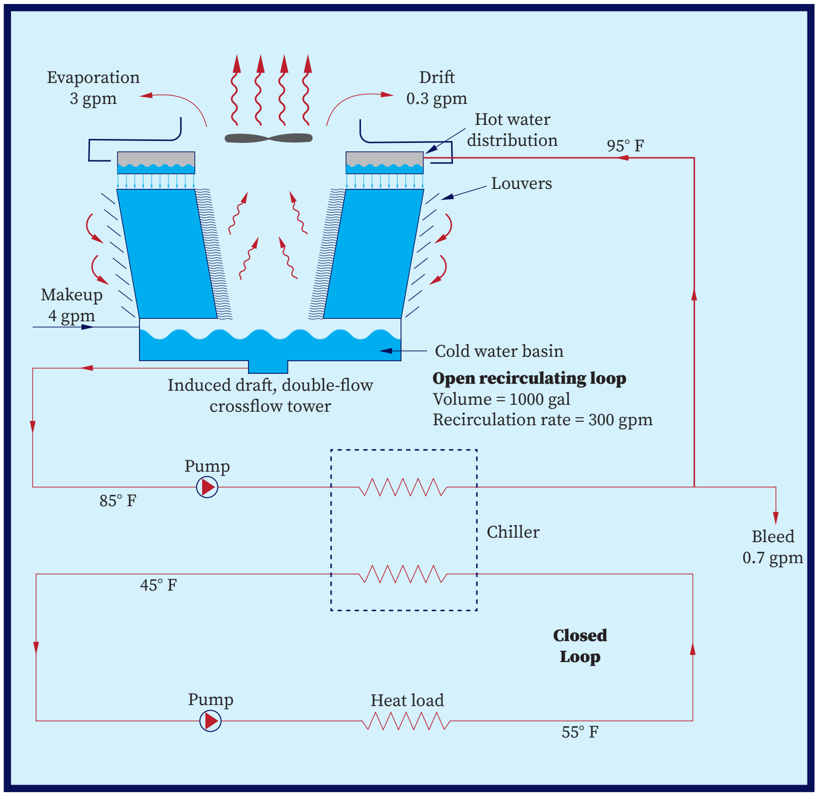
As the universal solvent, water is capable of dissolving a variety of materials as well as holding comparatively high concentrations of dissolved matter in solution. Over the ages, water has also provided a method for transporting materials from one place to another - sometimes as a result of natural flooding - frequently through the application of human ingenuity, e.g. shipping and canal/lock systems. Both ancient and modern manufacturing practices have taken advantage of both the solvent and transport capabilities of water. Another characteristic of water is the ability to collect, hold, and transport heat. Accordingly, the abundant volume of water on the earth's surface plays an important role in weather patterns and temperatures. The comparatively easy availability of water and its relatively low cost make it useful for comfort heating and cooling of buildings.



1 Simplified schematic of open recirculating and closed loops that provide comfort cooling to an office building.

The purpose of this article is to review the characteristics of water that impact its use in cooling water systems. Procedures and methods for coping with some of the solutes and particulates associated with water as they may impact a building's cooling water systems are discussed.

Water as heat transfer fluid

Swimmers and other water-sport enthusiasts are familiar with the role of water acting as a cooling agent as water evaporates from swimsuits or clothes. To cool a building, the same principle is used. Water is exposed to moving air so that a portion of the water evaporates, which results in cooling the remaining water. The open recirculating loop of the cooling system is comprised of the cooling tower and piping to and from the chiller or heat exchanger. Fig. 1 depicts an example of a 1000 gal open recirculating cooling loop where water collects heat from the chiller leaving the chiller at 95 F. Warm water pumped to the cooling tower falls about 10 ft to the basin of the cooling tower where the temperature is 85 F. The 10 F temperature change is the result of evaporation of about 3 gpm from the recirculating water. Recirculation rate (RR) is about 300 gpm; the entire volume of the 1000 gal system flows through the cooling tower every 3 min. A small percentage of the recirculation rate (RR = 300 gpm, in our example) is lost to drift or windage where the water leaves the cooling tower as a droplet rather than as a vapor. Mechanically intact drift or mist eliminators are important barriers to water leaving cooling towers as liquid. A mechanically intact, clean, cooling tower fill provides the necessary surface area so that air and water mix efficiently, and water leaves the cooling tower as water vapor and water droplet generation are minimized. For modern, high-efficiency cooling towers, drift is about 0.001 times the recirculation rate or about 0.3 gpm in our example. For older cooling towers or towers in poor repair with broken or missing drift eliminators or fill, more liquid is lost. At the extreme for water droplet loss is the spray pond that loses 0.025 times the recirculation rate or 7.5 gpm, if a spray pond replaced the cooling tower in our example. Note that only the water leaves the cooling tower by evaporation; the materials dissolved in the water remain behind. Conversely, water that leaves as liquid water droplets "drift" or "mist" can carry dissolved and particulate materials. In addition to the lost energy efficiency, cooling tower drift has been implicated as a source for Legionnaires' disease--hence, the importance of maintaining the cooling tower in excellent mechanical condition with intact fill and drift eliminators and a fan that is balanced and does not create additional droplets.

Since water is continuously being evaporated and lost as mist, makeup water must be added to the cooling tower--usually to the basin. The water level in the basin is controlled by a float valve so that entering makeup water is provided as needed. Because evaporation removes only water and not dissolved or particulate materials, evaporation cannot be done indefinitely without concomitant "bleed" or "blowdown." Bleed or blowdown is a controlled water loss from the system so that the dissolved materials do not accumulate in the cooling system. The amount of bleed required for a cooling system is heavily dependent upon the quality of the makeup water, particularly the calcium concentration. Bleed requirements and methods to control bleed are discussed below.

Table 1 shows the relationship of temperature and evaporation rates in our 1000 gal generalized cooling system It also shows the closed loop generally associated with cooling systems. The role of the closed loop is to circulate water through the air handlers or other heat-exchange devices (apparatus necessary to cool computer rooms is a good example) and collect waste heat by increasing the temperature of the water in the closed loop. The refrigeration cycle in the chiller transfers the heat to the open recirculating system where it is discharged to the atmosphere.

TABLE 1

Typical chemical analyses for water from three cities with hard water, moderately hard water, and soft water, respectively.

Parameter	San Antonio, TX well water	Cleveland, OH surface water	Potsdam, NY surface water
Alkalinity, M as $CaCO_3$	200	80	12
Hardness, total as $CaCO_3$	250	120	20
Hardness, calcium as $CaCO_3$	190	80	14
Hardness, magnesium as $CaCO_3$	60	40	6
Chloride, as Cl mg per L	180	20	9
Sulfate, as SO_4 mg per L	25	30	17
Silica, as SiO_2 mg per L	15	1	4
Conductivity mmhos	570	280	106
pH	7.0 to 7.3	7.1 to 7.5	7.2 to 7.4
Copper, mg per L	0.009	0.01	0.1
Iron, mg per L	0.001	0.02	0.1
Total organic carbon, as mg per L	N/A	2	3
Ammonia, as NH_3 mg per L	N/A	<0.01	<0.01
Nitrate, as NO_3 mg per L	2	1 to 3	3
Phosphate, total as PO_4	N/A	<0.01	10
Phosphate, ortho as PO_4	N/A	0.6	<1

N/A = Not Available

Water as solvent

A solute is a material that has been dissolved in a solvent. Solutes may be solids, liquids, or gases. Solvents frequently are liquids. When coffee is made, organic compounds extracted from the coffee grounds are the solutes, and water is the solvent. If sugar is added to coffee, the sugar is an additional solute. The coffee will contain many solutes--ions originally dissolved in the tap water used to make the coffee; numerous different organic compounds from the coffee beans; and the dissolved sugar, a well studied organic compound.

Concentrations of solutes in natural waters depend on the geology of the area in which the water is found. Some regions of the earth, such as the northeastern U.S., have igneous rock as the primary geological component from which soil was made over centuries of weathering. Other regions of the country have more sedimentary rock--limestone being the predominant example. Limestone is comprised primarily of calcium carbonate that can dissolve readily and produce "hard water." The hardness ions are calcium and magnesium, both of which are positively charged. Since charges must be balanced, negative charges must also be present. The predominant negative charges are carbonate and bicarbonate. Water flowing through regions of igneous rock tend to be soft waters containing relatively little calcium, magnesium, and carbonate. Since calcium, magnesium, and carbonate were found together so frequently and early chemical detection methods could not readily distinguish the three species, all three compounds today are expressed as $CaCO_3$ for many water treatment applications. Examples of hard water, moderate hardness water, and soft water are shown in Table 1. Note that total hardness as calcium carbonate is the sum of calcium hardness and magnesium hardness, both expressed as calcium carbonate. Since these materials can be dissolved from rock, it should not be unexpected that they would precipitate again from waters that contain appreciable concentrations to produce rock-like substances on surfaces.

Calcium carbonate deposits in pipes or heat-exchange surfaces can impede both water flow and heat exchange. Fig. 2A is an example of a scaled pipe with a decreased inner diameter. Decreasing the diameter of a pipe by having a calcium carbonate deposit slows down the water, allowing more calcium carbonate to deposit along the surface. Calcium carbonate deposits along tubing surfaces in heat exchangers or chillers insulate the water from the pipe and diminish heat transfer from the water to the pipe. If heat is not effectively transferred across the metal, it does not reach the refrigerant or other heat sink on the other side of the metal pipe. Higher energy costs and more equipment wear result. Fig. 2B shows pieces of scale that were deposited along a large diameter pipe. These "chips" are about 1 by 3 cm (0.5 by 1 in.) with the slight curvature of the large pipe where they were deposited before they broke off. Chips of this size can block flow through chiller tubing and clog distribution holes on cooling tower decks.

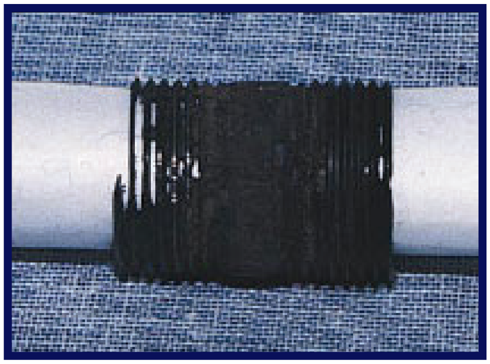
2A **A 2 in. diameter copper pipe lined with about 1 in. of scale.**

2B **Curved scale chips that broke away from a large diameter pipe.**

Additional solutes of interest in water treatment are chloride and sulfate. Chloride is used as a method to measure cycles of concentration. Historically, sulfate along with pH have been indicators of whether sulfuric acid was added to the system. Sodium and potassium are two other cations (positively charged solutes) found in natural waters. Sodium and potassium concentrations are not routinely monitored by water treaters because both are so soluble that precipitation with anions is rare. Also, atomic absorption spectroscopy is the usual way to quantify these two cations and easy field-test methods do not exist. Both are important contributors to conductivity measurements.

Silica can form silicate deposits particularly in boiler systems or heated loops. If silicate deposits are formed, removal is particularly difficult. Silica deposits are insulators. Glass fiber insulation is a silica deposit devised for its ability to minimize air movement and heat transfer. Having silica concentrations in the recirculating water at the expected levels demonstrates that silica deposits are not forming. Silica arrives in cooling systems with makeup water and particulate sand that are drawn into the cooling tower. Silicate is used as a component of some corrosion-inhibitor formulations.

Copper and iron in treated makeup waters are typically low, 0.1 mg per L or less. Some well waters may have 1 to 2 mg per L iron and are often treated by the municipality or well owner to remove the iron before the water is sent through the distribution system. Copper and iron are of interest in cooling systems as indicators of possible corrosion of copper and mild steel piping within the system. Elevated levels of copper and iron are more likely to be found in closed loops rather than open recirculating loops since the closed loop water remains longer with very small or no bleed and makeup water. Rather than checking levels of circulating dissolved metals, corrosion problems are more readily detected in open recirculating systems through the use of corrosion coupons. Corrosion coupons are metal samples of known weight placed in piping for one to three months, dried, and re-weighed. Fig. 3 shows a mild steel pipe with the threads lost to corrosion.



3 Corroded pipe threads. White paper rolled inside the pipe demonstrates that threads have been seriously corroded.

Many municipalities in the U.S. add chlorine to disinfect water. A residual chlorine concentration can often be found miles down the distribution system from the potable water plant--providing confidence that water- borne pathogens have been killed. A disadvantage of chlorine is that it reacts with dissolved organic compounds in the water to produce trihalomethanes, which have been implicated as carcinogens. Attempts to address this problem are two fold--minimize the dissolved organic compounds and minimize the chlorine added. Dissolved organic compounds in natural waters arrive from plants, animals, and microbes that live in or near lakes, reservoirs, and streams. Potable water facilities use a variety of chemicals and settling procedures to precipitate these materials and separate them from the water, prior to sending water to the distribution system. The result is that total organic carbon in potable systems is typically 5 mg per L or less. To minimize chlorine usage, one technique is to add about 0.5 mg per L ammonia to the distributed water. Ammonia and chlorine react to produce chloramines that have biocidal effects within water distribution systems. The chloramine produced results in less use of chlorine while still providing a chloramine residual within the distribution system.

The importance of this low concentration of ammonia to open recirculating cooling systems is probably small but has not been studied. The 0.5 mg per L ammonia in some makeup waters to cooling systems may be a source of nitrogen--a necessary nutrient for the microbial population. In closed loops comprised of copper piping, overdoses of ammonia may contribute to the corrosion of copper. When ammonia used as a refrigerant has leaked from refrigeration systems, nitrifying bacteria in the open recirculating cooling system convert ammonia to nitrate and acid that decreases system pH with corrosive results.

Nitrate is of concern for potable waters because concentrations higher than 15 mg per L can cause methemoglobinemia, which is “blue baby syndrome” in infants. Nitrate can serve as a necessary nitrogen source for microbial growth within a cooling system.

A variety of phosphates are added by municipalities to provide corrosion protection of the potable distribution system. For soft waters, phosphate is often an important component of a cooling water, corrosion-inhibitor formulation. In the cooling system, the possibility exists to produce calcium phosphate precipitates.

Organic compounds are materials that include carbon in their chemical structure. Plants, animals, and microbes are comprised primarily of carbon. Total organic carbon in potable waters is typically less than 5 mg per L and is probably the nutrient that is most limiting for microbial growth within the distribution system. In cooling towers, additional organic carbon can result from photosynthesis if algae are prominent, low concentrations of organic compounds are contributed by the water treatment program, and external sources discussed below.

pH is a measure of acidity of the water. Metals corrode more quickly at lower pH - 6.5 or less. pH of potable waters is typically 7 to 8. As evaporation occurs and alkalinity increases in open recirculating systems, the pH increases often to the 8.5 to 9 range. For closed loops, treatment often includes a buffer so that loop water is 8.5 to 9.5.

Conductivity is a measure of the electrical current through water. Pure water with no dissolved ions is an exceedingly poor conductor of electrical current. As concentrations of sodium, potassium, calcium, magnesium, carbonate, bicarbonate, phosphate, chloride, sulfate, and other charged materials increase, conductivity increases.

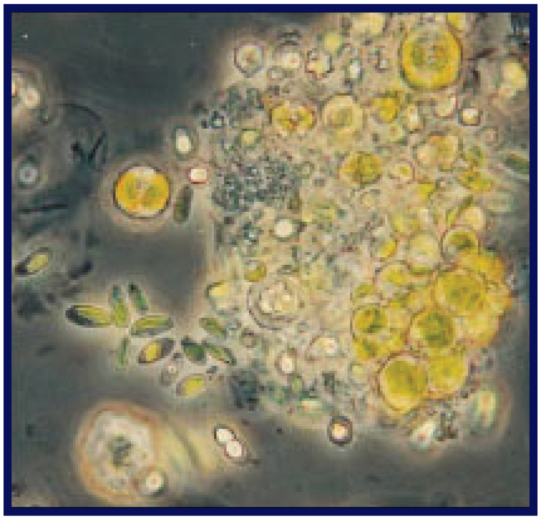
Additional sources

Makeup water for the cooling tower system serves as a source of soluble materials that may have the potential to precipitate within the cooling system. Other sources also exist, including the surrounding air, other nearby buildings, or local geology. A variety of airborne gases or particles can be drawn by a fan into the water as it falls through the cooling tower. Examples of gases include exhaust gases from kitchen vents; exhausts from automobiles, buses, or trucks; and gases from neighboring stacks. These gaseous carbon compounds dissolve in the water and can become nutrients for microbes. Organic solids that reach cooling systems include leaves and other plant debris and dead animals, such as birds, that are sometimes found in cooling systems. Plant and animal debris decompose, providing nutrients for microorganisms. Construction sites can provide substantial particulate matter that can be drawn into cooling systems that result in various muddy deposits on tube bundles or at low spots within the cooling water system. Generally, wind blown materials from construction sites are primarily inorganic (contain no carbon) such as clay, sand, and silt. These materials provide surfaces where organic compounds adsorb and microbes grow.

4A Composite photograph. Top--Fouled cooling tower fill. Fouling in this case was a variety of microbes and the slime they produced. Bottom--Clean cooling tower fill.

4B A variety of rod-shaped bacteria and two protozoans found in a recirculating cooling system.

Yet, another source of contamination of a cooling system is the system itself. Internal surfaces of piping, tube bundles, and cooling tower fill are all surface area that have the possibility to be colonized by bacteria that grow in biofilms along surfaces. The term biofilm is derived from bios, the Greek word for life. A film is a thin layer. Biofilms are comprised of the organisms and the sticky materials (mixtures of proteins, fats, and sugars) that they excrete. Biofilms occur in nature at interfaces between liquids, solids, and gases. In cooling systems, the biofilm particularly of interest occurs at a liquid-solid interface where pipes or cooling tower fill and water meet. Fig. 4A is an example of fouled and clean cooling tower fill. Under appropriate conditions, the biofilm sloughs off the surface, and bacteria and possibly protozoans are released to the recirculating water (Fig. 4B). Protozoans are single-celled organisms that eat bacteria and small particles. Other organisms important in cooling systems are algae that use sunlight energy to convert carbon dioxide and bicarbonate to algal cells (Fig. 4C). Protozoans can be thought of as "small animals," while algae are "small plants" in the cooling system environment. Bacteria are a separate group from protozoans and algae.



4C Two kinds of green algae with some bacteria found in a recirculating cooling system.

Goals of programs

The purpose of a water treatment program is to provide heat-exchange surfaces that are sufficiently intact and free of deposits so that design specifications are met. Cooling systems that are corroded with loss of piping, tube bundles, or pumps do not meet specifications. Cooling systems with scale do not meet specifications. (Calcium carbonate is a frequent example; other scales such as magnesium hydroxide, calcium phosphate, or scales containing silica can occur.) Cooling systems containing deposits of sand, silt, or organic material blown into the system by the wind do not meet specifications if these materials clog piping, strainers, cooling tower distribution holes, or tower fill or pumps. Profuse growth of microorganisms can prevent a cooling system from meeting heat-transfer specifications and may increase risk of legionellosis and other diseases.

Methods of treatment

As shown in Table 1, substantial variation among water from various geographical areas can occur. Water treatment formulations are devised to account for particular characteristics. Operating cycles of concentration are selected based on makeup water reaching the cooling system. Cycles of concentration is defined to be the ratio of chloride in the makeup to chloride concentration in the cooling system.

$$\text{Cycles of concentration} = \frac{[\mathrm{Cl}^-]_{system}}{[\mathrm{Cl}^-]_{makeup}}$$

Chloride is chosen because it is soluble and does not form precipitates as do calcium, magnesium, carbonate, phosphate, silicate, and occasionally other ions. Conductivity or any dissolved compound could theoretically be used in the calculation of the ratio, but chloride is chosen because of its high solubility. An exception to the use of chloride ion as the measure of cycles of concentration occurs if high levels of chlorine are used as a biocide. In this case, the cycles of concentration ratio would be high, and another parameter should be selected. To allow some safety margin, a maximum of 450 to 500 mg per L total hardness may be chosen, which means that the hard water example will have two cycles of concentration maximum, the medium hard water will have four cycles, and the soft water will have 20 cycles of concentration.

Scale control is the overriding concern in the hard water and a predominant concern in the medium hard water. In the soft water, corrosion is the major concern since very little hardness and alkalinity is present to raise the pH and buffer the water out of the corrosive range. In soft water regions of the country, phosphates are often the corrosion inhibitor of choice. In the soft water case in Table 1, 10 mg per L total phosphate is added polyphosphate--which the municipality uses to provide corrosion protection for metal pipes in the distribution system. An open recirculating cooling water formulation for this water is likely to include additional phosphate for corrosion control.

To control cycles of concentration, a conductivity meter continuously measures a moving sidestream of system water. The conductivity meter is connected to the bleed valve. As water evaporates and conductivity increases above a set point determined by building staff in cooperation with the local water treatment specialist, the bleed valve opens. Cycled water goes to drain, which may lower the level of water in the cooling tower basin. The float valve in the basin opens to replace the cycled bleed water with makeup water at one cycle of concentration. When conductivity decreases below another set point, the bleed valve closes. Table 1 shows that in Cleveland, for example, the set points selected may be 1500 micromhos per cm to open bleed valve and 1200 micromhos per cm to close the bleed valve. On-site or laboratory testing of the water constituents, such as hardness, alkalinity, chloride, and conductivity, are done to check that the conductivity meter and bleed control valve are working and appropriately calibrated. The ratio of chloride in system to chloride in makeup should be about the same as the ratio for hardness in the system and in the makeup. If differences are substantial and occur consistently, someone (building staff and water treatment specialists) should be looking for a reason.

Cooling water treatment formulations are primarily designed to minimize scale and corrosion and may help with deposition control. Typical components of water treatment formulations include one or more of several phosphonates, polymers, and azoles. The phosphonates play a dual role in both corrosion control and calcium carbonate modification so that more calcium carbonate stays in solution rather than precipitating on surfaces. The polymers are important as conditioning agents so that calcium carbonate crystals are mixed with the polymer and do not form a crystalline structure. The azoles provide a film along copper surfaces and minimize copper corrosion.

Biocides are used in cooling systems to minimize microbial fouling, including bacterial and algal growth. In the U.S., biocides are registered by the federal Environmental Protection Agency (EPA) and by most of the individual states. Manufacturers of biocides submit a registration package to the EPA that includes information on use applications (cooling systems, process waters, brewery pasteurizers, decorative fountains, etc.) and concentrations proposed for use. This information is included on the biocide label. It is against the law to use a biocide for a purpose that is not stated on the label or at concentrations not allowed on the label.

Human contact with biocides should be minimized. Use of pumps and timers, eductors, various types of feeders, or other methods of dosing is a more responsible approach to putting the biocide in the cooling system than manual dosing, which was extremely popular in the 1970s. Substantial improvement in this aspect of cooling system management has occurred in the last two decades.

Biocides are classified in two categories: oxidizing and non-oxidizing. Oxidizing biocides include ozone, chlorine, bromine, iodine, and several organic molecules that donate chlorine and/or bromine when they dissolve. Ozone requires an on-site generator that may use either dry air or pure oxygen. The cost of the generator is a significant part of the water treatment program. Chlorine has been used extensively and is one of the least expensive biocides available. Chlorine is available as gaseous chlorine, a liquid sodium hypochlorite, and a solid calcium hypochlorite. As pH increases above pH 7, hypochlorous acid, HOCl, is converted to hypochlorite ion OCl- , which has less efficacy than the HOCl. Use of chlorine is usually avoided in systems that have stainless steel since the chloride ion is corrosive to stainless steel. The bromine equilibrium between hypobromous acid, HOBr, and hypobromite ion, OBr-, allows use of bromine at pH 8.5 to pH 9 where many open recirculating cooling systems operate. Iodine was developed for use in small volume cooling systems that otherwise may not be treated at all. Cooling tower makeup water flows through a feeder containing iodine pellets that dissolve over several months or a cooling season.

Non-oxidizing compounds include an assortment of organic materials that have been selected over the last four or five decades based on their efficacy against target microbial populations. These compounds are substantially less toxic for non-targeted fish, bird, plant, and mammal populations. Most of the non-oxidizers are available as a liquid formulation that can be dosed to the cooling system with a small pump controlled by a timer so that the biocide is dosed once or twice per week. An alternating biocide dose scheme may dose one biocide one week and a second another week. The purpose is to avoid selection of a population of microbes resistant to a particular biocide. Selection for antibiotic-resistant populations of disease causing bacteria is well known in medicine and pharmacy.

Biocide selection criteria include: local water chemistry; metallurgy used in the system; what equipment is available - pumps, timers, feeders for solid bromine, ozone generator, etc.; staff available to oversee the equipment and treatment program; what has worked in this system in the past; what works in similar systems in the local area; and price.

Over the years, a variety of mechanical separation units have been effectively used, including various types of strainers, filters, and centrifugal separators. “Pigs” (metal cylinders or brushes slightly smaller than the tube diameter) that periodically travel up and down chiller tubes are another example of mechanical cleaning. Any physical removal of particulates, such as sand, silt, green plant materials (leaves, air-borne plant fibers, etc.) rags, plastic bags, or dead animals is beneficial. Removal of these materials decreases the food and surface area available to the microbes. The result is that both the biocides and the corrosion/scale inhibitors can do a better job for a system that is physically clean than for a fouled system.

Monitoring and documentation

Quantitative information needed to decide whether the system is meeting heat transfer design specifications is difficult to generate because design conditions may not occur. Occasions frequently occur when the system is operating at partial load. Monitoring methods can range from visual observations and periodic testing by the maintenance staff to on-line continuous monitoring of multiple parameters by various analytical instruments controlled by a computer.

At a minimum, OSHA Material Safety Data Sheets should be reviewed by people who are responsible for or associated with chemical application. A log book recording chemical determinations--chloride, hardness, and product concentrations--should be kept and periodically reviewed. Records of additional tests such as corrosion coupon analyses should be filed and reviewed. If conditions in the building change--new construction, excess vacancy, or other changes--reconsider the treatment program and the methods for monitoring.

Conclusion

An effective water treatment program depends upon a knowledge of the local water chemistry, selection of an appropriate scale/corrosion-inhibitor package and biocide for the local water, and consistent application and monitoring of the treatment program.

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