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THE METRO HANDBOOK

OF WATER TREATMENT FOR HVAC SYSTEMS

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1 INTRODUCTION

This book discusses the technology of treating water for use in commercial and industrial heat-transfer equipment, with specific emphasis on heating, ventilating, and air-conditioning (HVAC) systems. Additionally, this book includes an overview of the environmental maintenance and surveillance of water systems, including cooling towers and evaporative condensers, in view of the now significantly increased awareness of the risks of infection that may result from systems that are poorly designed and dirty and or badly maintained.

It should be noted that the risks of infection (from bacterial organisms such as *Legionella sp.*) are not limited to cooling systems, but can emanate from almost any type of building facilities water systems, including domestic hot and cold water services, pools, spa baths, showers and humidifier pans. (Similarly, it is recognized that risks of infection may also develop in all types of air handling and ventilation systems that are likewise poorly maintained or not cleaned on a regular basis. In air handling systems, infection and related problems typically involves mold organisms such as *Aspergillus sp.* or *Stachybotrus sp.*, the same organisms that can proliferate behind damp sheetrock walls and insulation). However, it is beyond the scope of this book to discuss in any great detail the environmental maintenance, surveillance and infection control of facilities water and air systems. Additionally, it is also beyond the scope of this book to cover all aspects of industrial and process water treatment, since specific designs for each type of process are generally required. For fuller coverage of industrial water treatment, see the references and bibliography at the end.

1.1 Why Water Treatment?

Water treatment for corrosion and deposit control is a specialized technology. Essentially, it can be understood when one first recognizes why treatment is necessary to prevent serious failures and malfunction of equipment, which uses water as a heat-transfer medium. This is seen more easily when one observes the problems water can cause, the mechanism by which water causes these problems, which leads to solutions, and the actual solutions or cures available.

Water is a universal solvent. Whenever it comes into contact with a foreign substance, there is some dissolution of that substance. Some substances dissolve at faster rates than others, but in all cases a definite interaction occurs between water and whatever it contacts. It is because of this interaction that problems occur in equipment such as boilers or cooling-water systems in which water is used as a heat-transfer medium. In systems open to the atmosphere, corrosion problems are made worse by additional impurities picked up by the water from the atmosphere.

Most people have seen the most obvious examples of corrosion of metals in contact with water and its devastating effect. Corrosion alone is the cause of failure and costly replacement of equipment and is itself a good reason why water treatment is necessary.

1.1.1 Cost of Corrosion

The direct losses due to corrosion of metals for replacement and protection are reported to be at least \$20 to \$25 billion annually in the U.S. alone; over \$8 billion is spent for corrosion-resistant metallic and plastic equipment, almost \$5 billion for protective coatings, and over \$1 billion for corrosion inhibitors (year 2000 dollars). All this is just to minimize the losses due to corrosion! Typical examples of these losses resulting from failures of piping, boiler equipment, and heat-exchanger materials because of corrosion and deposits are depicted in this chapter.

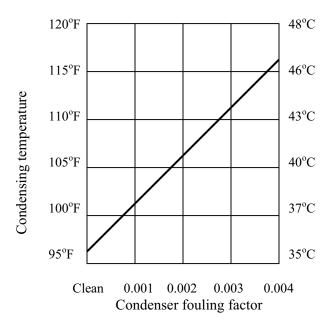


FIGURE 1.1 Effect of Scale on Condensing Temperature

Only with good design and correct application water treatment programs, including corrosion inhibitors, will HVAC equipment, such as heating boilers and air-conditioning chillers and condensers, provide maximum economical service life. However, even more costly than failures and replacement costs, and less obvious, is the more insidious loss in energy and operating efficiency due to corrosion, fouling and deposits.

In heat-transfer equipment, corrosion and deposits will interfere with the normal efficient transfer of heat energy from one side to the other. The degree of interference with this transfer of heat in a heat exchanger is called the *fouling factor*. In the condenser of an air-conditioning machine, a high fouling factor causes an increase in condensing temperature of the refrigerant gas and thus an increase in energy requirements to compress the refrigerant at that higher temperature. The manufacturer's recommended design fouling-factor for air-conditioning chillers and condensers is 0.0005. This means that the equipment cannot tolerate deposits with a fouling factor greater than 0.0005 without the efficiency of the machine being seriously reduced.

Figure 1.1 graphically illustrates the effect of scale on the condensing temperature of a typical water-cooled condenser. From this graph, we see that the condensing temperature increases in proportion to the fouling factor. An increase in condensing temperature requires a proportionate increase in energy or compressor horsepower to compress the refrigerant gas. Thus the fouling factor affects the compressor horsepower and energy consumption, as shown in figure 1.2.

Condenser tubes are quickly fouled by a hard water supply, which deposits calcium carbonate on the heat-transfer surface. The explanation of the mechanism of this type of fouling is given in a later section.

Table 1.1 lists the fouling factors of various thicknesses of a calcium carbonate type of scale deposit most frequently found on condenser watertube surfaces where no water treatment or incorrect treatment is applied. The additional energy consumption required to compensate for a calcium carbonate type of scale on condenser tube surfaces of a refrigeration machine is illustrated in Figure 1.3. The graph shows that a scale thickness of only 0.025 in (0.635 mm) [fouling factor of 0.002] will result in a 22 percent increase in energy consumption, which is indeed wasteful.

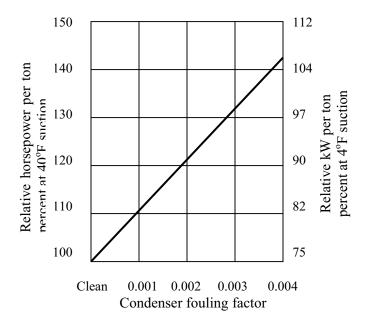


FIGURE 1.2 Effect of Scale on Compressor Horsepower

1.1.2 Cost of Scale and Deposits

The actual cost of scale is even more surprising. For example, a 500-ton air conditioning plant operating with a scale deposit of 0.025 in (0.635 mm) of a calcium carbonate type will increase energy requirements by 22 percent if the same refrigeration load is maintained and cost approx.\$4752 in additional energy consumption required for only 1 month (720 h) of operation. This is based on an efficient electric- drive air-conditioning machine's requiring 0.75 kW/(h ton) of refrigeration for compressor operation. Note: the average cost for this energy in early 2000 was 8.0 cents/kWh., thus: $(500 \times 720 \times 0.22 \times $0.08 \times 0.75 = $4752)$.

With proper care and attention to water treatment, wasteful use of energy can be avoided. Likewise, in a boiler operation for heating or other purposes, an insulating scale deposit on the heat-transfer surfaces can substantially increase energy requirements.

Boiler scale or deposits can consist of various substances including iron, silica, calcium, magnesium, carbonates, sulfate, and phosphates. Each of these, when deposited on a boiler tube, contributes in some degree to the insulation of the tube.

TABLE 1.1 Fouling Factor of Calcium Carbonate Type of Scale

Approximate thickness of calcium carbonate type of scale, in (mm)	Fouling factor
0.000 0.006 (0.1524) 0.012 (0.3048) 0.024 (0.6096)	Clean 0.0005 0.0010 0.0020
0.036 (0.9144)	0.0030

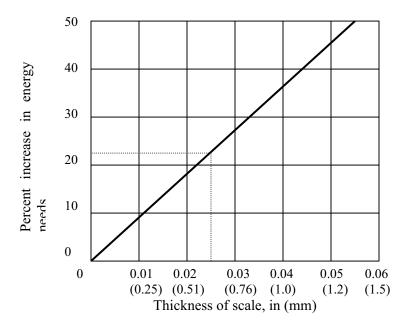


FIGURE 1.3 Effect of Condenser Tube Scale on Energy Consumption, $K = 1.0 \text{ Btu/(h/ft}^3/^{\circ}\text{F})$. Example: Scale that is 0.025 in (0.6 mm) Thick Requires an Increase in Energy of 22 Percent.

That is, the deposits reduce the rate of heat transfer from the hot gases or fire through the boiler metal to the boiling water. When this occurs, the temperature of the boiler tube metal increases. The scale coating offers a resistance to the rate of heat transfer from the furnace gases to the boiler water. This heat resistance results in a rapid rise in metal temperature to the point at which the metal bulges and blisters and eventually, a failure results. This is the most serious effect of boiler deposits, since failure of such tubes causes boiler explosions.

Table 1.2 shows the average loss of energy as a result of boiler scale. A normal scale of only 1/16-in (1.588-mm) thickness can cause an energy loss of 4 percent. For example, a loss of 4 percent in energy as a result of a scale deposit can mean that 864 gal (3270.6 L) more of No. 6 fuel oil than is normally used would be required for the operation of a steam boiler at 100 boiler hp (bhp) (1564.9 kg) for 1 month (720 h).

TABLE 1.2 Boiler Scale Thickness vs. Energy Loss

Normal scale, calcium carbonate type, in (mm)	Dense scale (iron silica type)	Energy loss, %
1/32 (0.794)	1/64 (0.397)	2
1/16 (1.588)	1/32 (0.794)	4
3/32 (2.381)	3/64 (1.191)	6
1/8 (3.175)	1/16 (1.588)	8
3/16 (4.763)	3/32 (2.381)	12
1/4 (6.350)	1/8 (3.175)	16



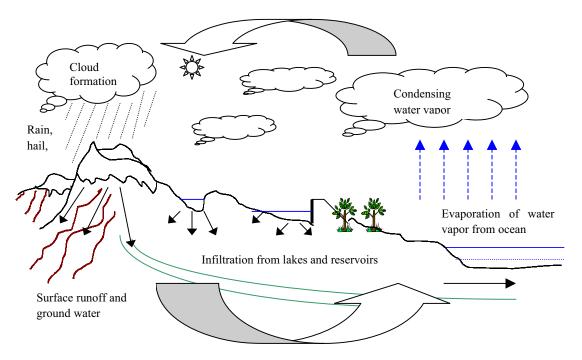


FIGURE 1.4 Hydrologic Cycle

The costs of additional fuel due to efficiency losses can easily run into many thousands of dollars each year.

The need for water treatment, therefore, is to ensure the various contaminants and dissolved minerals do not cause operational problems in the waterside of HVAC equipment. The potential risks and costs involved are closely linked to the sources of water used. And these, in turn, are a function of local ecosystems and the hydrologic cycle. Figure 1.4 shows the cycle and it is discussed in the next chapter, as part of water chemistry.

2 WATER CHEMISTRY

Water and its impurities are responsible for the corrosion of metals and formation of deposits on heat-transfer surfaces, which in turn reduce efficiency and waste energy. Having seen the effects of corrosion and deposits, let us see how this can be prevented. The path to their prevention can best be approached through understanding their basic causes, why and how they occur.

Water, the common ingredient present in heat-transfer equipment such as boilers, cooling towers, and heat exchangers, contains many impurities. These impurities render the water supply more or less corrosive and/or scale forming.

2.1 Hydrologic Cycle

The hydrologic cycle (figure 1.4) consists of three stages: evaporation, condensation, and precipitation. This cycle begins when the rays of the sun heat surface waters on the earth, which vaporize and rise into the troposphere, a thin layer of air and moisture approximately 7 mi (11 km) thick surrounding the earth. Clouds of condensed moisture form in the troposphere and when carried over land by the wind, they contact cold-air currents. This causes precipitation or rain or snow. In this manner, water returns to the earth's surface, only to repeat the cycle. Throughout the hydrologic cycle, the water absorbs impurities. While falling through the atmosphere, water dissolves the gases, oxygen, nitrogen, carbon dioxide, nitrogen oxides, sulfur oxides, and many other oxides present in the atmosphere in trace amounts.

The quantity of these gases in the atmosphere depends on the location. For example, in large urban areas rainwater often contains high concentrations of carbon dioxide, sulfur oxides, and nitrogen oxides. In rural areas, water contains lesser amounts of these gases. Studies made have noted that in the recent past the acidity of our rainfall has steadily increased. This is caused by the increased amounts of sulfur and nitrogen oxide gases that pollute the atmosphere (acid rain).

TABLE 2.1 Reactions of Water with Minerals

Hydrolysis is the chemical reaction between water and minerals in which the mineral dissolves in the water:

NaCl +	$H_2O \rightarrow$	Na ⁺ +	C1 ⁻ +	H_2O
sodium	water	sodium ion	chloride ion	water
chloride		in solution	in solution	

Hydration is the absorption of water by minerals, changing the nature of the mineral:

 $CaSO_4 + H_2O \rightarrow CaSO_4 \cdot H_2O$ calcium water calcium sulfate sulfate hydrate





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CERTIFICATE OF ANALYSIS - VARIOUS WATER ANALYSES

LOCATION	1	2	3	4	5
PARAMETER					
рН	6.9	7.4	7.7	7	7.6
P ALKALINITY, as CaCO ₃ mg/l					
BICARBONATES, as CaCO₃mg/l	12	85	90	30	300
CARBONATES, as CaCO ₃ mg/l					
HYDROXIDES, as CaCO₃ mg/l	12	85	90	30	300
M (TOTAL) ALKALINITY, as CaCO ₃ mg/l					
TOTAL HARDNESS, as CaCO ₃ mg/l	16	132	140	60	454
SULFATE, as SO ₄ mg/l					
SILICA, as SiO ₂ mg/l	1.5	1	7	14.3	9.5
IRON, as Fe mg/l	TRACE	0	0	0.07	0
CHLORIDE, as NaCl mg/l	13	21	41	29	58
SPECIFIC CONDUCTANCE microS/cm					
TOTAL DISSOLVED SOLIDS mg/l	33.5	148	195	106	514
MOLYBDATE, as Na ₂ MoO ₄ mg/l					
PHOSPHATE, as PO ₄ mg/l					
SULFITE, as Na ₂ SO ₃					

1 = New York, NY: Croton Reservoir 2 = Syracuse, NY: Otisco Lake

3 = Washington, D.C.:Potomac River

4 = Jamica, NY: wells

5 = Yellow Springs, OH: wells

FIGURE 2.2 Typical Analyses of Surface Waters and Underground Well Waters.



2.2 Water Impurities

In contact with the earth surface, rainwater will tend to dissolve and absorb many of the minerals of the earth. The more acidic the rainfall, the greater the reaction with the earth's minerals. This reaction includes hydrolysis and hydration. As water passes over and through gypsum, calcite, dolomite, and quartz rock, it will dissolve calcium, silica, and magnesium minerals from these rocks (table 2.1). In similar manner, other minerals present in the earth's crust can be dissolved and taken up by the water. Table 2.2 shows some of the minerals present in the earth's surface, which by reaction with water dissolve and become impurities in water. Water accumulates on the earth's surface in lakes, rivers, streams, and ponds and can be collected in reservoirs. These surface water supplies usually contain fewer minerals but more dissolved gases. Underground water supplies are a result of surface waters' percolating through the soil and rock. The water supplies usually contain large quantities of minerals and not much dissolved gases, although there are numerous exceptions to this general rule. Table 2.3 lists the various sources of water. Figure 2.2 show typical analyses of surface waters and underground well waters. A brief observation of the analyses of these different water supplies shows that the natural impurities and mineral content do indeed vary with location. In fact, many well water supplies in a very proximate location exhibit vast differences in mineral content. Let us examine each of the basic impurities of water to see how they contribute to corrosion and deposits.

2.3 Dissolved Gases

Oxygen. One of the gases in the atmosphere is oxygen, which makes up approximately 20 percent of air. Oxygen in water is essential for aquatic life; however, it is the basic factor in the corrosion process and is, in fact, one of the essential elements in the corrosion process of metals. Therefore, dissolved oxygen in water is important to us in the study of corrosion and deposits.

Carbon Dioxide. Carbon dioxide is present in both surface and underground water supplies. These water supplies absorb small quantities of carbon dioxide from the atmosphere. Larger amounts of carbon dioxide are absorbed from the decay of organic matter in the water and its environs. Carbon dioxide contributes significantly to corrosion by making water acidic. This increases its capability to dissolve metals. Carbon dioxide forms the mild carbonic acid when dissolved in water, as follows:

$$CO_2$$
 + H_2O \rightarrow H_2CO_3 carbon water carbonic dioxide acid

Sulfur Oxides. Sulfur oxide gases are present in the atmosphere as a result of sulfur oxides absorbed from the atmosphere, in which they are present as pollutants from the combustion of fuels containing sulfur, such as coal and fuel oil. In large urban areas, the quantity of sulfur oxides that are absorbed by surface water supplies and aerated waters used in cooling towers can be significant. Also when dissolved in water, sulfur oxides form acids which create a corrosive atmosphere.

$$SO_3$$
 + H_2O \rightarrow H_2SO_4
sulfur water sulfuric
trioxide acid



Nitrogen Oxides. Nitrogen oxides are also present in the atmosphere both naturally and from pollutants created by the combustion process. These too form acids, when absorbed by water, and contribute to the corrosion process.

3NO ₂ +	$H_2O \rightarrow$	$2HNO_3 +$	NO
nitrogen	water	nitric	nitric
dioxide		acid	oxide

Hydrogen Sulfide. The odor typical of rotten eggs, which is found in some water, is due to the presence of hydrogen sulfide. This gas comes from decaying organic matter and from sulfur deposits. Hydrogen sulfide forms when acidic water reacts with sulfide minerals such as pyrite, an iron sulfide commonly called "fool's gold":

FeS	+	$2H^{+}$	+	\rightarrow	Fe^{2+}	+	H_2S
ferric		acid			iron		hydrogen
sulfide		in soluti	on		in solution	on	sulfide

Hydrogen sulfide reacts with water to form hydrosulfuric acid, a slightly acidic solution. Its presence in water is also due to the decomposition of organic matter and protein, which contain sulfur. Hydrogen sulfide is also a constituent of sewer gas, marsh gas, and coal gas. It can be present in water and also comes from these sources. Because of its acidic reaction in water, hydrogen sulfide is very corrosive and must be removed or neutralized.

2.4 Dissolved Minerals

Alkalinity. Alkalinity is the quantity of dissolved alkaline earth minerals expressed as calcium carbonate. It is the measured carbonate and bicarbonate minerals calculated as calcium carbonate since that is the primary alkaline earth mineral contributing to alkalinity. Alkalinity is also measured and calculated as the hydroxide when that is present. All natural waters contain some quantity of alkalinity. It contributes to scale formation because its presence encourages deposition of calcium carbonate, or lime scale.

pH Value. The *quality* of alkalinity, or the measure of the relative strength of acidity or alkalinity of a water is the pH value, a value calculated from the hydrogen-ion concentration in water. The pH scale ranges from 0 to 14.

TABLE 2.2 Mineral Groups

Mineral:	Found as:
Silicates	Quartz, augite, mica, chert, feldspar, hornblende
Carbonates	Calcite, dolomite, limestone
Halides	Halite, fluorite
Oxides	Hematite, ice, magnetite, bauxite
Sulfates	Anhydrite, gypsum
Sulfides	Galena, pyrite
Natural elements	Copper, sulfur, gold, silver
Phosphates	Apatite



A pH of 7.0 is neutral. It indicates a balance between the acidity and alkalinity. As the pH decreases to zero, the alkalinity decreases and the acidity increases. As the pH increases to 14, the alkalinity increases and the acidity decreases. The pH scale (figure 2.3) is used to express the strength or intensity of the acidity or alkalinity of a water solution. This scale is logarithmic so that a pH change of lunit represents a tenfold increase or decrease in the strength of acidity or alkalinity. Hence water with a pH value of 4.0 is 100 times more acid in strength than water with a pH value of 6.0. Water is corrosive if the pH value is on the acidic side. It will tend to be scale-forming if the pH value is alkaline.

Hardness. Hardness is the total calcium, magnesium, iron, and trace amounts of other metallic elements in water, which contributes to the "hard" feel of water. Hardness is also calculated as calcium carbonate, because it is the primary component contributing to hardness. Hardness causes lime deposits or scale in equipment. It is present dissolved in water as silicate or suspended in very fine, invisible form as colloidal silica.

Iron, Manganese, and Alumina. These dissolved or suspended metallic elements are present in water supplies in varying quantities. They are objectionable because they contribute to a flat metallic taste and form deposits. These soluble metals, when they react with oxygen in water exposed to the atmosphere, form oxides which precipitate and cause cloudiness, or "red water." This red color, particularly from iron, causes staining of plumbing fixtures, sinks, and porcelain china and is a cause of common laundry discoloration.

Silica. Silica is dissolved sand or silica-bearing rock (such as quartz) through which the water flows. Silica is the cause of very hard and tenacious scales that can form in heat-transfer

Chlorides. Chlorides are the sum total of the dissolved chloride salts of sodium, potassium, calcium, and magnesium present in water. Sodium chloride, which is common salt, and calcium chloride are the most common of the chloride minerals found in water. Chlorides do not ordinarily contribute to scale since they are very soluble. Chlorides are corrosive, however, and cause excessive corrosion when present in large volume, as in seawater.

TABLE 2.3 Sources of Water

Туре:	Examples:
Surface water	Lakes and reservoirs of fresh water
Ground water	Water below the land surface caused by surface
	Runoff, drainage and seepage
Water table	Water found in rock saturated with water just
	above the impervious layer of the earth
Wells	Water-bearing strata of the earth –water seeps and
	drains through the soil surface, dissolving and
	absorbing minerals of which the earth is composed
	(thus, the higher mineral content of most well waters)



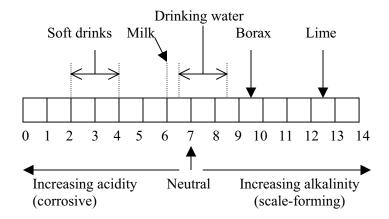


FIGURE 2.3 The pH scale

Sulfates. Sulfates are the dissolved sulfate salts of sodium, potassium, calcium, and magnesium in the water. They are present due to dissolution of sulfate-bearing rock such as gypsum. Calcium and magnesium sulfate scale is very hard and difficult to remove and greatly interferes with heat transfer.

Total Dissolved Solids. The total dissolved solids (TDS) reported in water analyses are the sum of dissolved minerals including the carbonates, chlorides, sulfates, and all others that are present. The dissolved solids contribute to both scale formation and corrosion in heat-transfer equipment.

Suspended Matter. Suspended matter is finely divided organic and inorganic substances found in water. It is caused by clay silt and microscopic organisms, which are dispersed throughout the water, giving it a cloudy appearance. The measure of suspended matter is turbidity. Turbidity is determined by the intensity of light scattered by the suspended matter in the water.

3 CORROSION

Corrosion is the process whereby a metal through reaction with its environment undergoes a change from the pure metal to its corresponding oxide or other stable combination. Usually, through corrosion, the metal reverts to its naturally occurring state, the ore. For example, iron is gradually dissolved by water and oxidized by oxygen in the water, forming the oxidation product iron oxide, commonly called rust. This process occurs very rapidly in heat-transfer equipment because of the presence of heat, corrosive gases and dissolved minerals in the water, which stimulate the corrosion process.

The most common forms of corrosion found in heat-transfer equipment are

- General corrosion
- Oxygen pitting
- Galvanic corrosion
- Concentration cell corrosion
- Stress corrosion
- Erosion-corrosion
- Condensate grooving
- Microbiologically influenced corrosion (MIC)

3.1 General Corrosion

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

In boilers, general corrosion is observed in the total overall disintegration of the tube metal surface in contact with the boiler water. General corrosion occurs when the process takes place over the entire surface of the metal, resulting in a uniform loss of metal rather than a localized type of attack. It is often, but not always, accompanied by an accumulation of corrosion products over the surface of the metal. Iron and other metals are corroded by electrochemical reaction resulting in the metal going into solution in the water. It is necessary, therefore, to limit corrosion of these metals by reducing the activity of both hydroxyl ions and hydrogen ions, i.e., by maintaining a neutral environment. Another important factor in the corrosion process is dissolved oxygen. The evolution of hydrogen gas in these reactions tends to slow the rate of the corrosion reaction and indeed, in many instances, to stop it altogether by forming an inhibiting film on the surface of the metal which physically protects the metal from the water.

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

3.2 Oxygen Pitting

The second type of corrosion frequently encountered in heat-transfer equipment is pitting.



```
Anodic reactions: Cathodic reactions:

1. Fe \rightarrow Fe<sup>++</sup> + 2e<sup>-</sup>
2. Fe<sup>++</sup> + 2OH<sup>-</sup> \rightarrow Fe(OH)<sub>2</sub>
2. 2H<sup>+</sup> + 2e<sup>-</sup> \rightarrow H<sub>2</sub>↑

3. 4Fe(OH)<sub>2</sub> + O<sub>2</sub> + 2H<sub>2</sub>O \rightarrow 4Fe(OH)<sub>3</sub>

H<sub>2</sub> O \Leftrightarrow OH<sup>-</sup> + H<sup>+</sup>

\downarrow O<sub>2</sub> \uparrow Fe<sup>++</sup>
\downarrow O<sub>2</sub>

H<sub>2</sub>O Fe electron flow \rightarrow 2e<sup>-</sup> Fe H<sub>2</sub>O
```

FIGURE 3.1 Corrosion Reactions Forming Rust Blisters Over Pit

Pitting is characterized by deep penetration of the metal at a small area on the surface with no apparent attack over the entire surface as in general corrosion.

The corrosion takes place at a particular location on the surface, and corrosion products frequently accumulate over the pit. These appear as a blister, tubercle, or carbuncle.

Oxygen pitting is caused by dissolved oxygen. It differs from localized pitting due to other causes, such as deposits of foreign matter. Figure 3.1 shows the reactions taking place at a pit site caused by dissolved oxygen. Oxygen pitting occurs in steam boiler systems where the feedwater contains dissolved oxygen. The pitting is found on boiler tubes adjacent to the feedwater entrance, throughout the boiler, or in the boiler feedwater line itself.

One of the most unexpected forms of oxygen pitting is commonly found in boiler feedwater lines following a deaerator. It is mistakenly believed that mechanically deaerated boiler feedwater will completely prevent oxygen pitting. However, quite to the contrary, water with a low concentration of dissolved oxygen frequently is more corrosive than that with a higher dissolved oxygen content. This is demonstrated by the occurrence of oxygen pitting in boiler feedwater lines carrying deaerated water.

Mechanical deaerators are not perfect, and none can produce a feedwater with zero oxygen. The lowest guaranteed dissolved oxygen content that deaerators produce is 0.005 cm³/L. This trace quantity of dissolved oxygen is sufficient to cause severe pitting in feedwater lines or in boiler tubes adjacent to the feedwater entrance. This form of pitting is characterized by deep holes scattered over the surface of the pipe interior with little or no accumulation of corrosion products or rust, since there is insufficient oxygen in the environment to form the ferric oxide rust.

3.3 Galvanic Corrosion

Corrosion can occur when different metals come in contact with one another in water. When this happens an electric current is generated similar to that of a storage battery.

The more active metal will tend to dissolve in the water, thereby generating an electric current (an electron flow) from the less active metal. A coupling of iron and copper, as in Figure 3.2 develops this current.



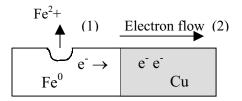


FIGURE 3.2 Galvanic corrosion caused by dissimilar-metal couple.

- (1) Iron going into solution loses two electrons: $Fe^0 \rightarrow Fe^{2+} + 2e^{-}$
- (2) Electrons flow to copper, the less reactive metal

This tendency of a metal to give up electrons and go into solution is called the "electrode potential."

In galvanic corrosion, commonly called "dissimilar-metal corrosion," there are four essential elements:

- 1. A more reactive metal called the "anode"
- 2. A less reactive metal called the "cathode"
- 3. A water solution environment called the "electrolyte"
- 4. Contact between the two metals to facilitate electron flow

The rate of galvanic corrosion is strongly influenced by the electrode potential difference between the dissimilar metals. The galvanic series is a list of metals in order of their activity, the most active being at the top of the list and the least active at the bottom. The further apart two metals are on this list, the greater will be the reactivity between them and, therefore, the faster the anodic end will corrode. The galvanic series is shown in figure 3.3.

If one or more of these four essential elements are eliminated, the corrosion reactions will be disrupted and the rate of corrosion slowed or halted altogether.

One method of preventing this type of corrosion is to eliminate contact of dissimilar metals in HVAC equipment by using insulating couplings or joints, such as a dielectric coupling which interferes with the electron flow from one metal to the other. Other forms of protection involve the removal of dissolved oxygen and use of protective coatings and inhibitors, which provide a barrier between the corroding metal and its environment.

3.4 Concentration Cell Corrosion

Concentration cell corrosion is a form of pitting corrosion that is a localized type of corrosion rather than a uniform attack. It is frequently called "deposit corrosion" or "crevice corrosion" since it occurs under deposits or at crevices of a metal joint.

Deposits of foreign matter, dirt, organic matter, corrosion products, scale, or any substance on a metal surface can initiate a corrosion reaction as a result of differences in the environment over the metal surface. Such differences may either be differences of solution ion concentration or dissolved oxygen concentration. With concentration cell corrosion, the corrosion reaction proceeds as in galvanic corrosion since this differential also forms an electrode potential difference. Maintaining clean surfaces can best prevent this form of corrosion.



Metals and	Standard Electrode
Alloys	Potential (mV)
anodic/ base end	
 Magnesium & magnesium alloys 	-2300 to -1350
 Zinc & galvanizing 	-850 to -750
 Aluminum & Al alloys 	-700 to -350
• Cadmium	\pm -650
• Carbon steel & cast iron (Fe/C/Si etc.)	-550 to -400
• Lead & tin-lead solders	-325 to -250
 Nickel & Ni resist alloys 	-250 to +100
• Stainless steels (Fe/Cr/Ni etc.)	-50 to +200
• Copper & brasses (Cu/Zn etc.)	-50 to +50
• Hydrogen	0
• Bronzes, Al & Ni/Al bronzes (Cu/Sn etc.)	± 0
 Cupro-nickels 	0 to $+50$
• Chromium (passive)	±50
Hastelloys/ Monel/ Inconel	±100
• Titanium	±150
cathodic/ noble end	

FIGURE 3.3 Practical galvanic series

3.5 Stress Corrosion

Stress corrosion is a combination of exposure of a metal to a corrosive environment and application of stress on the metal.

It is frequently seen on condenser tubes and boiler tubes in the area where the tubes are rolled into the tube sheets. In steam boilers, stress corrosion has been referred to as "necking and grooving." It is seen as a circumferential groove around the outside of a firetube where it enters the tube sheet.

The corrosion failure is a result of a corrosive environment and stresses and strains at the point of failure. Usually it occurs at the hottest end of the tube at the beginning of the first pass against the firewall. It concentrates at the tube end because of strains from two sources. First, when tubes are rolled in, stresses axe placed on the metal, expanding the metal to fit the tube sheet. Second, when a boiler is fired, the heat causes rapid expansion of the tube, and consequently strains are greatest at the tube ends, which are fixed in the tube sheets. This actually causes a flexing and bowing of the tube, and sometimes the expansion is so severe that the tubes loosen in the sheets. During this bending of the tube, the natural protective iron oxide film forming at the tube ends tends to tear or flake off, exposing fresh steel to further attack. Eventually, the tube fails due to both corrosion and stress.

Stress corrosion can also occur on condenser tubes and heat-exchanger tubes from heat expansion that causes stresses in the metal at tube supports or tube sheets. This problem is reduced by more gradual firing practices in boilers, which allow more gradual temperature changes, and by using proper inhibitors to correct the corrosive environment.



3.6 Erosion-Corrosion

"Erosion-corrosion" is the gradual wearing away of a metal surface by both corrosion and abrasion. It is also commonly called "impingement corrosion."

Water moving rapidly through piping can contain entrained air bubbles and suspended matter, sand, or other hard particulates. This is not uncommon in cooling tower waters where such particles are washed from the atmosphere.

These abrasive particles remove natural protective oxide films present on the surface of the metal and cause general corrosion of the exposed metal. The higher the velocity of the impinging stream, the greater the rate of erosion-corrosion.

3.7 Condensate Grooving

Condensate grooving is a particular phenomenon of steam condensate line corrosion in HVAC equipment. It is found in steam condensate piping on all types of equipment, heat exchangers, steam-turbine condensers, unit heaters, steam absorption condensers, radiators, or any type of unit utilizing steam as a heat-transfer medium.

Condensate grooving is a direct chemical attack by the steam condensate on the metal over which it flows and is identified by the typical grooves found at the bottom of the pipe carrying the condensate. *The primary cause of condensate grooving is carbon dioxide*. The dissolved carbon dioxide forms a mild carbonic acid. The methods available to prevent this type of corrosion include removal of bicarbonate and carbonate alkalinity from the boiler makeup water (dealkalization) and use of carbonic acid neutralizers and filming inhibitors.

3.8 Microbiologically Influenced Corrosion (MIC)

Since the early 1 980s the phenomenon of Microbiologically Influenced Corrosion (MIC) has become as a very serious problem in building HVAC recirculating water systems. MIC is the term given to corrosion involving the reaction of microbiological species with metals. It is corrosion caused or influenced by microbiological organisms or organic growths on metals. There are many forms and mechanisms of MIC involving many types of microbiological organisms.

The basic causes of MIC found in recirculating water systems are as follows:

- Iron Related Bacteria (IRB)
- Sulfate Reducing Bacteria (SRB)
- Acid Producing Bacteria (APB)
- Biological Deposits

Iron Related Bacteria (IRB). A major group of organisms that are a direct cause of corrosion of iron and steel in recirculating water systems is the iron related bacteria (IRB), such as Gallionellea ferrugine and Ferrobacillus sp. This class of organisms is responsible for causing corrosion of iron and steel by direct metabolism of iron. Some of these organisms actually consume iron by using it in their metabolic process and then deposit it in the form of hydrated ferric hydroxide along with the mucous secretions. Iron bacteria are commonly found in all types of cooling system, especially in low flow areas.

Sulfate Reducing Bacteria (SRB). The best-known group of organisms involved in MIC is the Sulfate Reducing Bacteria (SRB).



This group of organisms basically falls into three kinds, the *Desulfovibrio*, *Desulfotomaculum*, and *Desulfomonas* genera of organisms, all of which metabolize sulfur in one form or another. All are anaerobic (they live without directly metabolizing oxygen). The most widely known organism is the *Desulfovibrio* and is often found in cooling systems, especially where oil, or sludge is present.

Acid Producing Bacteria (APB). Another group of bacteria that cause MIC is the Acid Producing Bacteria (APB). There are many types of APB most of which are the slime forming bacteria such as *Pseudomonas*, *Aerobacter*, and *Bacillus* types which exude various organic acids in their metabolic process. Organic acids such as formic acid, acetic acid and oxalic acid have been identified in deposits of slime containing APB. These organic acids cause low pH conditions at local sites, resulting in corrosion at these sites.

One APB that is commonly responsible for MIC is the *Thiobacillus*. These organisms oxidize sulfur compounds forming sulfuric acid, which is extremely corrosive and leads to localized under-deposit and pitting corrosion, often resulting in pinholes in pipework.

Biological Deposits (BD). MIC can also be caused by other forms of organic growths such as algae, yeast, molds, and fungus along with bacterial slimes. Even in the absence of specific corrosive organisms such as the IRB, SRB or APB biological deposits provide the environment for corrosion through establishment of concentration cells resulting in under deposit corrosion. Biological deposits in general act as traps and food for other organisms resulting in rapid growth. This complex matrix sets up a corrosion potential between adjacent areas of a metal surface that may have a different type of deposit.

To control MIC it is important to understand the processes that cause it and therefore understand how to prevent it. It is clear that an essential control program will include control of all types of biological growths in recirculating water systems.

4. SCALE AND SLUDGE DEPOSITS

The most common and costly water-caused problem encountered in HVAC equipment is scale formation. The high cost of scale formation stems from the significant interference with heat transfer caused by water mineral scale deposits.

4.1 Mineral Scale and Pipe Scale

At this point, we should differentiate between mineral scale and pipe scale. *Mineral scale* is formed by supersaturation and deposition of the more insoluble minerals naturally present in water, the heat-transfer medium is the name given to the formation of natural iron oxide coating or corrosion products that form on the interior of piping (especially during construction projects where the pipe may be exposed to the elements), which can flake off and appear as a scale.

Mineral scale in steam boilers, heat exchangers, and condensers consists primarily of calcium carbonate, the least soluble of the minerals in water. Other scale components, in decreasing order of occurrence, are calcium sulfate, magnesium carbonate, iron, silica, and manganese. Present also in some scales are the hydroxides of calcium, magnesium, and iron as well as the phosphates of these minerals, where phosphates and alkalinity are used as a corrosion or scale inhibitor. Sludge is a softer form of scale and results when hard-water minerals reacting with phosphate and alkaline treatments forming a soft, paste-like substance rather than a hard, dense material. In most cases, scales contain a complex mixture of mineral salts because scale forms gradually and deposits the different minerals in a variety of forms.

The major cause of mineral scale is the inverse solubility of calcium and magnesium salts. Most salts or soluble substances, such as table salt or sugar, are more soluble in hot water than in cold. Calcium and magnesium salts, however, dissolve more readily and in greater quantity in cold water than in hot, hence inverse solubility. This unique property is responsible for the entire problem of mineral scale on heat-transfer surfaces in HVAC equipment.

From this property alone, we can readily understand why mineral scale forms on hot water generator tubes, condenser tubes, boiler tubes, etc. It is simply the fact that the hottest surface in contact with the water is the tube surface of this type of equipment.

In condenser water systems using recirculating cooling tower water or once-through cooling water, the water temperature is much lower than that in steam boiler or hot-water systems. At these lower temperatures most of the scale-forming minerals will remain in solution, but the tendency will be to deposit calcium carbonate on the heat-transfer surfaces where there is a slight rise in temperature. The primary factors that affect this tendency are:

- Alkalinity
- Hardness
- pH
- Total dissolved solids
- Temperature

The higher the alkalinity of a particular water, the higher the bicarbonate and/or carbonate content. As these minerals approach saturation, they tend to come out of solution.

Likewise, a higher concentration of hardness will increase the/tendency of calcium and magnesium salts to come out of solution. The pH value reflects the ratio of carbonate to bicarbonate alkalinity.



 $\mathbf{pH_S} = 12.3 - (\log_{10}\mathbf{Ca} + \log_{10}\mathbf{TA} + 0.025\mathbf{Temp} - 0.011\mathbf{TDS}^{1/2})$

Where: Ca = Calcium Hardness as ppm CaCO₃.

TA = Total Alkalinity as ppm CaCO₃.

Temp = Temperature as °C.

TDS = Total Dissolved Solids ppm.

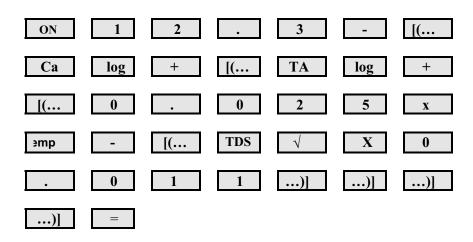


FIGURE 4.1 Sequence of calculator keys to press for solving pH_S of calcium carbonate

The higher the pH value, the greater the carbonate content of the water. Since calcium carbonate and magnesium carbonate are less soluble than the bicarbonate, they will tend to precipitate as the pH value and carbonate content increase.

Also affecting this tendency are the total dissolved solids and temperature. The higher the solids content, the greater the tendency to precipitate the least soluble of these solids. The higher the temperature, the greater the tendency to precipitate the calcium and magnesium salts because of their property of inverse solubility.

4.2 Langelier Saturation Index (LSI)

The Langelier index is a *calcium carbonate saturation index* that is very useful in determining the scaling or corrosive tendencies of a water. It is based on the assumption that any given water with a scaling tendency will tend to deposit a corrosion-inhibiting film of calcium carbonate and hence will be less corrosive. By inference, a water with a non-scaling tendency will tend to dissolve protective films and be more corrosive. This is not entirely accurate since other factors are involved in corrosion, as we have seen in the section on corrosion, but, although a relatively simple tool, it provides a valuable index in determining the tendency of a water to directly influence scaling or corrosive actions.

In the 1950s, Eskell Nordell arranged five basic variables into an easy-to-use chart to quickly determine the pH of saturation of calcium carbonate and the Langelier index. This index is based on the pH of saturation of calcium carbonate.

The pH of saturation (or "saturation pH", pH_s) of calcium carbonate is the theoretical pH value of any particular water if that water is saturated with calcium carbonate.

As, for example, the actual pH of a recirculating water approaches or even exceeds the pH of saturation of calcium carbonate under certain specific conditions; the tendency is to form a scale of calcium carbonate. If the actual pH is well below the pH of saturation of calcium carbonate, the tendency is to dissolve minerals and therefore to be corrosive. The Langelier index of a recirculating water, therefore, is determined by comparing the actual pH with the saturation pH of calcium carbonate under the same specified conditions.

To determine the Langelier index, the actual pH of the water must be measured, and the pH of saturation of calcium carbonate is calculated from a measure of the *total alkalinity*, *hardness*, *total dissolved solids*, and *temperature* (see Figure 4.1 above).

Once the pH of saturation of calcium carbonate has been calculated, the Langelier saturation index (LSI) can be determined from the formula.

$$LSI = pH - pH_s$$

A positive index indicates scaling tendencies; a negative one, corrosion tendencies, The guide shown in table 4.1 indicates the extent of these tendencies.

4.3 Ryznar Index (Ryznar Stability Index) (SI)

Another useful tool for determining the tendencies of water is the Ryznar index. This index is also based on the pH of saturation of calcium carbonate and was intended to serve as a more accurate index of the extent of scaling or corrosion in addition to the tendency. This index was derived from the LSI by observation of actual cooling water conditions and is calculated as follows:

Ryznar Index =
$$2(pH_s)$$
 - pH

Where $pH_s = pH$ of saturation of calcium carbonate, as calculated from Figure 4.1, and pH = actual measured pH of the water. Table 4.2 can be used to determine the tendency and extent of corrosion or scaling with the Ryznar index.

Let us see how these indices can help us in analyzing a particular water supply.

TABLE 4.1 Prediction of Water Tendencies by using the LSI

Langelier Saturation Index	Tendency of Water
+3.0	Extremely scale forming
+2.0	Strongly scale forming
+1.0	Scale forming
+0.5	Uncertainty zone, scale/pitting corrosion possible
-1.0	Corrosive
-2.0	Strongly corrosive
-3.0	Extremely corrosive



Figure 2.2 (Typical Analyses of Surface Waters and Underground Well Waters) depicts an analysis report on the Washington, DC water supply. The Langelier saturation index at 50°F (10°C) is determined by using this analysis and the data shown on Figure 4.1 as follows:

$$pH_s = 9.3 + A + B - (C + D)$$

= 9.3 + 0.1 + 2.3 - (1.8 + 2.0)
= 8.2

and

$$LSI = pH - pH_s = 7.7 - 8.2 = -0.5$$

From table 4.1, according to the Langelier saturation index, this water supply is "slightly corrosive" and, therefore non-scale-forming. In fact, it is in an "uncertainty zone", where there is no clear indication of scale or corrosion, and the likelihood is that both phenomena will occur, although not to any strong degree. Typically, the LSI uncertainty zone extends from +0.5 to -0.5. A very high tendency for scale is indicated by perhaps +3.0 and strong corrosion by perhaps -3.0.

To learn more about this water, the Ryznar index (SI) can be calculated in the same manner:

$$SI = 2(pH_s) - pH = 16.4 - 7.7 = 8.7$$

According to Table 4.2 this water supply tendency indicates it is "strongly corrosive." The Ryznar index, being more quantitative, indicates that the degree of corrosion would be greater than we would anticipate from the tendency shown by the qualitative Langelier saturation index.

In practice, the SI often tends to give "worst-case" scenario, when compared to LSI and may range from +3.0 (strongly scaling) to, perhaps, +10 or +11 (extremely corrosive). Thus, in an examination of a water supply, often both the Langelier and the Ryznar indices are used to determine the scale-forming or corrosion tendencies.

In open cooling tower condenser water systems and steam boilers, however, there is a constant accumulation of minerals as a result of evaporation of pure water, such as distilled water, and makeup water containing the various mineral impurities. Therefore, in these systems the pH, concentration of hardness, total dissolved solids, and alkalinity are constantly changing, making a study of the Langelier and Ryznar indices relatively complex and potentially subject to gross inaccuracies. These indices are useful indicator tools but other indicators should also be employed, such as Mass Balance checks on total minerals in (from makeup water) compared to total minerals out (with the bleed water).

TABLE 4.2 Prediction of Water Tendencies by using the Ryznar SI

Ryznar Stability Index	Tendency of Water
<4.0	Extremely scale forming
4.0-5.0	Strongly scale forming
5.0-6.0	Scale forming
6.0-7.0	Uncertainty zone, scale/pitting corrosion possible
7.0-8.0	Corrosive
8.0-9.0	Strongly corrosive
>9.0	Extremely corrosive



4.4 Boiler Scale

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

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

4.5 Condenser Water Scale

In recirculating cooling tower condenser water systems for air conditioning and refrigeration chillers, scale deposits are a direct result of precipitation of the carbonate, calcium sulfite, or silica minerals due to such an over-concentration of these minerals that their solubility or pH of saturation is exceeded and the minerals come out of solution.

Scale in this equipment can include foreign substances such as corrosion products, organic matter, and mud or dirt. These are usually called 'foulants' rather than "scale." Treatment to prevent mineral scale should, therefore, include sufficient dilution of the recirculating water to prevent the concentration of minerals from approaching the Saturation point, ph control to prevent the pH from reaching the pH of saturation of calcium carbonate, and chemical treatments to inhibit and control scale crystal formation.



5 FOULANTS

In addition to water mineral scale, other deposits of mud, dirt, debris, foreign matter, and organic growth are a recurrent problem in recirculating water systems. Deposits of foreign matter plug narrow passages and interfere with heat transfer and foul heat-transfer surfaces, causing inefficient performance of the equipment and higher energy consumption that otherwise necessary.

5.1 Mud, Dirt, and Clay

Open recirculating cooling tower systems are most subject to deposits of mud, dirt, and debris. A cooling tower is a natural air washer with water spraying over slats and tower fill washing the air blown through either naturally or assisted by fans. Depending on the location, all sorts of airborne dust and debris end up in cooling tower recirculating water systems. These vary from fine dust particles to pollen, weeds, plant life, leaves, tree branches, grass, soil, and stones. The fine particles of dust and dirt tend to collect and compact in the condenser water system, especially in areas of low circulation. At heat-transfer surfaces, the dust and dirt can deposit and compact into a sticky mud and seriously interfere with operating efficiency.

Muddy foulants are a common occurrence and form with the combination of airborne particles, corrosion products, scale, and organic matter. Very rarely can one identify a foulant as a single compound because it is usually a complex combination of all these things.

In closed recirculating water systems, foulants are not nearly as varied and complex as in open systems, but they are just as serious when they occur. Deposits in closed systems are usually caused by dirt or clay entering with the makeup water or residual construction debris. A break in an underground water line can result in dirt, sand, and organic matter being drawn into a system and is a common source of fouling.

Makeup water containing unusual turbidity or suspended matter is usually treated at the source by coagulation, clarification, and filtration so as to maintain its potability. Suspended matter and turbidity, therefore, are not common in makeup water in HVAC systems since the makeup water usually comes from a municipal or local source, over which there is a water authority responsible for delivery of clear, potable water. Where a private well water, pond, or other nonpublic source of water is available for use as makeup water to recirculating water systems and boilers, it should be carefully examined for turbidity and suspended matter. The suspended matter measured as turbidity should be no more than the maximum of 1 turbidity unit for drinking water recommended by the Environmental Protection Agency. When the supply is excessively turbid, some form of clarification such as coagulation, settling, filtration, and/or fine strainers should be used to remove the suspended matter and reduce the turbidity to below 1 unit.

The more common problem with suspended matter and turbidity results from makeup water that is temporarily or occasionally dirty. This may occur when the local water authority is cleaning sections of a distribution main or installing new mains or when water mains are cut into during some nearby construction project. This kind of work creates a disturbance of the water mains, causing settled and lightly adherent pipeline deposits to break off and be flushed into the water supply. These deposits consist mostly of iron oxide corrosion products and dirt, clay, or silt.

5.2 Black Mud and Mill Scale

One of the most common and difficult foulants found in closed systems is a black mud made up of compacted, fine, black magnetic iron oxide particles.



This black mud not only deposits at heat-transfer surfaces, but also clogs or blocks narrow passages in unit heaters, fan-coil units, and cooling, reheat, and heating coils in air- handling units. This black mud is a result of wet very fine particles of black magnetic iron oxide being compacted into a dense adherent mud.

The interior of black iron piping, commonly used for recirculating water, has a natural black iron oxide protective coating ordinarily held intact by oil-based inhibitors used to coat the pipe to prevent corrosion during storage and lay-up. This natural iron oxide protective coating is called *mill scale*, a very general term which can be applied to any form of pipe scale or filings washed off the interior of the pipe. This mill scale film becomes disturbed and disrupted during construction due to the constant rough handling, cutting, threading, and necessary battering of the pipe. After construction, the recirculating water system is filled and flushed with water, which removes most of the loosened mill scale along with any other construction debris. However, very fine particles of magnetic iron oxide will continue to be washed off the metal surface during operation, and in many instances this washing persists for several years before it subsides. Mill scale plugging can be a serious problem. It is best alleviated in a new system by thorough cleaning and flushing with a strong, low-foaming detergent-dispersant cleaner. This, however, does not always solve the problem. Even after a good cleanout, gradual removal of mill scale during ensuing operation can continue.

5.3 Boiler Foulants

In steam boilers, foulants other than mineral scale usually consist of foreign contaminants present in the feedwater. These include oil, clay, contaminants from a process, iron corrosion products from the steam system, and construction debris in new boiler systems. Mud or sludge in a boiler is usually a result of scale-forming minerals combined with iron oxide corrosion products and treatment chemicals. Such foulants are commonly controlled by using modern polymeric dispersants, which prevent adherence on heat-transfer surfaces.

In heating boilers, the most frequent foulants other than sludge are oil and clay. Oil can enter a boiler system through leakage at oil lubricators, fuel oil preheaters, or steam heating coils in fuel oil storage tanks. When oil enters a boiler, it causes priming and foaming by emulsifying with the alkaline boiler water. Priming is the bouncing of the water level that eventually Cuts the boiler off at low water due to the very wide fluctuation of this level. Oil can also carbonize at hot boiler tubes, causing not only serious corrosion from concentration corrosion cells but also tube ruptures as a result of overheating due to insulating carbon deposits. Whenever oil enters a boiler system, it must be removed immediately to prevent these problems. This is usually done by blowing down the boiler heavily, and often, by additionally "boiling out" with an alkaline detergent cleaner.

Clay is a less frequent foulant in boilers, but it, too, can form insulating deposits on tube surfaces. Clay enters a boiler with the boiler makeup water that is either turbid or contaminated with excessive alum, used as a coagulant in the clarification process. Clay can be dispersed with the use of dispersants in the internal treatment of the boiler, but makeup water should be clear and free of any turbidity before it is used as boiler feedwater. Where turbidity and clay are a constant problem, filtration of the boiler feedwater is in order.

5.4 Construction Debris

All new systems become fouled and contaminated with various forms of foreign matter during construction.



It is not uncommon to find these in the interior of HVAC piping and heat exchangers: welding rods, beads, paper bags, plastic wrappings, soft drink can rings, pieces of tape, insulation wrappings, glass, and any other construction debris imaginable.

It is necessary not only to clean out construction debris from the interior of HVAC systems prior to initial operation, but also to clean the metal surfaces of oil and mill scale naturally present on the pipe interior. This oil and mill scale, as has been shown, can seriously foul and plug closed systems and cause boiler tube failures, if the oil is carbonized during firing. Every new recirculating water system and boiler must be cleaned thoroughly with a detergent-dispersant type of cleaner or, as in steam boilers, with an alkaline boilout compound. This initial cleanout will remove most of the foulants and prevent serious operational difficulties.

5.5 Organic Growths

Organic growths in HVAC equipment are usually found in open recirculating water systems such as cooling towers, air washers, and spray coil units. Occasionally closed systems become fouled with organic slimes due to foreign contamination. Open systems are constantly exposed to the atmosphere and environs, which contain not only dust and dirt but also innumerable quantities of microscopic organisms and bacteria. Cooling tower waters, because they are exposed to sunlight, operate at ideal temperatures, contain mud as a medium and food in the form of inorganic and organic substances, and are a most favorable environment for the abundant growth of biological organisms. Likewise, air washers and spray coil units, as they wash dust and dirt from the atmosphere, collect microscopic organisms, which then tend to grow in the recirculating water due to the favorable environment. The organisms that grow in such systems consist primarily of algae, fungi, and bacterial slimes.

5.6 Algae

Algae are the most primitive form of plant life and together with fungus form the family of thallus plants. Algae are widely distributed throughout the world and consist of many different forms. The forms found in open recirculating water systems are the blue-green algae, green algae, and brown algae. The blue-green algae, the simplest form of green plants, consist of a single cell and hence are called unicellular. Green algae are the largest group of algae and are either unicellular or multicellular. Brown algae are also large, plantlike organisms that are multicellular.

Large masses of algae can cause serious problems by blocking the air in cooling towers, plugging water distribution piping and screens, and accelerating corrosion by concentration cell corrosion and pitting. Algae must be removed physically before a system can be cleaned since the mass will provide a continuous source of material for reproduction and biocides will be consumed only at the surface of the mass, leaving the interior alive for further growth.

5.7 Fungi

Fungi are also a thallus plants similar to the unicellular and multicellular algae. They require air, water, and carbohydrates for growth. The source of carbohydrates can be any form of carbon. Fungi and algae can grow together; the algae living within the fungus mass are furnished with a moist, protected environment, while the fungus obtains carbohydrates from the algae.

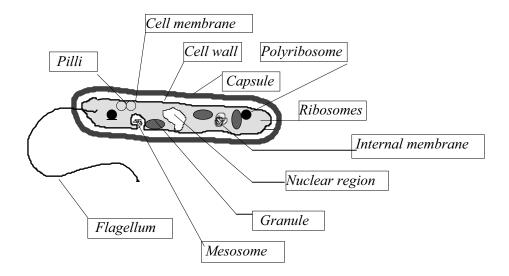


FIGURE 5.1 Bacterial Cell Identifying Principal Structures

5.8 Bacteria

Bacteria are microscopic unicellular living organisms that exhibit both plant and animal characteristics. They exist in rod-shaped, spiral and spherical forms. There are many thousands of strains of bacteria, and all recirculating waters contain some bacteria. The troublesome ones, however, are bacterial slimes, iron bacteria, sulfate- reducing bacteria, and pathogenic bacteria. Control is by developing a program of addition of pesticides, called Microbiocides, or simply biocides.

There are many different types, both oxidizing and non-oxidizing, which are discussed later in this chapter. For a general structure see figure 5.1 above.

5. 9 Pathogenic Bacteria

Pathogenic bacteria are disease-bearing bacteria. Cooling tower waters, having ideal conditions for the growth of bacteria and other organisms, can promote the growth of pathogenic bacteria, which may then give rise to infection and possibly death (such as in cases of growth of Legionella organisms and the development of Legionnaires Disease).

In very many instances around the world, where operating conditions are right (temperature, pH, etc.) and cleaning and maintenance is poor pathogenic bacteria have been found growing in cooling tower waters. Therefore, it is as important to keep these systems clean and free of bacterial contamination, to inhibit growth of pathogenic bacteria, as it is to prevent growth of slime-forming and corrosion-promoting bacteria. All cooling systems should be drained, cleaned and disinfected at least twice per 12 month period, irrespective of whether the cooling systems operate on a summer cycle only or all-year-round. In addition to good maintenance, a surveillance program should also be instituted and all records kept in a logbook.

Often, a risk assessment program is an additional and necessary precaution prior to starting up a new or winterized tower, or where design or location is suspect (e.g. poor drift elimination, or the tower is sited too close to a ventilation system fresh air intake).



5.9.1 Legionnaires' Disease and Pontiac Fever

These diseases are both forms of Legionellosis, are caused from the inhalation, by susceptible individuals, of certain serotypes (varieties) of the Gram-negative bacilli, *Legionella pneumophila*, and also by some other species/serotypes. The mode of transmission is usually through water droplets containing the organism.

Cooling systems with open recirculating cooling towers, or evaporative condensers, along with other types of equipment which can produce a water aerosol, that have not been properly designed, cleaned or maintained, may easily create the growth conditions required for transmission. Organisms can also be found in building, potable water storage and distribution systems, such as hot water storage tanks (calorifiers), especially those designs that permit stratification of hot stored water and cold makeup water. Also, spa baths, hydrotherapy pools and others.

Legionellosis is a type of pneumonia. It was first identified after the 1976 Convention of the American Legion in Pennsylvania, when over two hundred people were taken ill and thirty-four subsequently died. The species most commonly associated with disease outbreaks is *Legionella pneumophila serotype 1*, which appears to be the most pathogenic of the genus.

Legionnaires' Disease is frequently characterized as an "opportunistic" disease, meaning that it most frequently attacks individuals who have an underlying illness or have weakened immune systems. Good control over cooling systems in hospital and other healthcare premises are therefore, particularly important, in order to control infection risks.

At its onset, Legionnaires' Disease is characterized by a high fever, chills, headaches, and muscular pain. A dry, non-productive, cough develops and most patients suffer breathing difficulties. A third of the patients suffer from diarrhea and/or vomiting and half become confused or delirious. (In outbreaks, typically the fatality rate is around 20%). Although most people make a complete recovery, some can suffer long-term symptoms.

If recognized in its early stages, the disease can be effectively treated with antibiotics. Legionnaires Disease is much more common than generally thought. Although significant efforts are now made to regularly clean and maintain water systems, the organism is ubiquitous and many cases of Legionnaires Disease still occur each year. Unfortunately most cases still go undiagnosed and, where identified, these may result in considerable adverse publicity.

Pontiac Fever: Legionella bacteria may also cause other forms of Legionellosis such as Pontiac Fever, which is a short, self-limiting, flu-like illness, which has no long-term effects. Pontiac Fever develops rapidly, (5 hours to 3 days) and lasts for 3 to 5 days. (The attack rate is high, typically some 95%). It produces headaches, nausea, vomiting, aching muscles, and a cough but no pneumonia develops.

Aerosol formation is the consequence of the normal operation of evaporative condensers, cooling towers and certain domestic water services equipment such as shower/ spray systems. Bacteria from these water systems may be inhaled whenever an aerosol is produced, increasing the risk of exposure.

Poor water-system designs, installations, maintenance and management are typically associated with the illness and fatalities, and therefore usually preventable.

However it has to be said that, there is no evidence that well managed and maintained cooling systems provide any significant risk of exposure to Legionellosis. The consequence of regulations for the control of Legionella organisms in cooling systems and other water systems (and the penalties that could be imposed) has meant, and continues to mean, that the control of Legionella has become an even more important consideration for many engineers, water treatment managers and the water management industry as a whole.



6 PRETREATMENT EQUIPMENT

Prior to internal treatment of HVAC equipment, it is frequently necessary to use mechanical equipment to remove from the feedwater supply damaging impurities such as dissolved oxygen, excess hardness, or suspended solids.

The choice of proper equipment and its need can be determined by studying the quality and quantity of makeup water used in a boiler, condenser water system, and an open or a closed recirculating water system.

6.1 Water Softeners

Hardness in the makeup water is the cause of scale formation. In equipment using large volumes of hard water, a substantial amount of scale can form on heat-transfer surfaces in a short time. In these circumstances, it may be economical to remove the hardness from the water supply before it is used in the equipment.

Determining the Need for Water Softeners. In open cooling tower condenser water, evaporative condensers, and surface spray units, removal of the hardness with pretreatment equipment is usually not economical. These systems operate at pH values close to the neutral point, where the hardness can be kept in solution with the aid of antiscalants and pH control types of chemical treatments. This treatment will be required even if most of the hardness is removed. Therefore, it is not economically advantageous to install water softeners in this equipment unless the makeup water is so hard that it cannot be used at all in the particular system without some form of pretreatment to at least partially soften the water.

Waters with a hardness of more than 300 or 400 mg/L require some form of pretreatment to partially soften the water so that it can be used for cooling tower makeup water. Likewise, it is not economical to install water-softening equipment on closed chilled-water and low-temperature hot-water heating systems since such systems use very little makeup water and internal treatment with antiscalants can prevent scale on heat-transfer surfaces.

With steam and high-temperature hot-water boilers, however, removal of hardness from the makeup water is frequently required. The determining factor usually is the quality of available makeup water. With high-temperature hot-water boilers, if the hardness of the makeup water exceeds 100 mg/L, the initial fill and makeup water should be softened to remove the hardness and prevent excessive scale or sludge deposits on heat-transfer surfaces.

With steam boilers, the determining factors are both the hardness and the amount of makeup water used. In low-pressure heating applications where steam is used for heating only and possibly small amounts of humidification requiring less than 10 percent of the steam generated, the boiler feedwater will consist of 90 percent or more of return steam condensate. In instances such as this, the makeup water will not require external hardness removal since the small amount of hardness entering the system can be controlled with internal treatment.

In steam boiler systems that use more than 10 percent raw makeup water, it may prove economical and practical to install a water softener. Usually if the makeup water in these systems exceeds 100 mg/L hardness and the amount of makeup water is more than 1000 gal/day (3785 L/day), a water softener will be required. This can be justified by comparing the cost of internally treating the boiler water to control scale and sludge deposits with the operating cost of an external water softener

Another useful guideline is that if the hardness of water entering a boiler exceeds 1000 gr/h, a water softener usually is required.

Note: grains per hour are determined by multiplying the hardness in grains-per-gallon (17.1 mg/L per 1.0 gr/gal) by the makeup rate in gallons per hour:

Grains per hour = hardness, gr/gal x makeup, gal/h

Ion-Exchange Water Softeners. The type of water softener used for boiler makeup water is a synthetic zeolite softener containing an ion-exchange water softener resin. This ion-exchange resin adsorbs calcium and magnesium ions from the water passing over the resin bed. The resin at the same time releases sodium, hence the term "ion exchange."

The size of the softener required depends on the rate of makeup water and the amount of hardness to be removed. The softener should have a minimum delivery rate of 6.6 gal/mm (25.2 L/min) per 100 bhp [3450 lb/h (1564.9 kg/h) steam rate].

6.2 Dealkalizers

Another ion-exchange water conditioner that may be required is the dealkalizer. A steam boiler that operates with makeup water containing excessive quantities of carbonate and bicarbonate alkalinity not only will develop excess alkalinity in the boiler (causing priming, foaming, and carryover), but also will generate large quantities of carbon dioxide as a result of decomposition of the carbonates and bicarbonates. This process results in an acid steam and condensate, which, as noted previously, causes severe corrosion of steam and condensate return lines.

The alkalinity in these cases can be reduced by 90 percent by passing the makeup water through a dealkalizer following the water softener. Usually a dealkalizer cannot be economically justified unless the total alkalinity as calcium carbonate exceeds 100 mg/L and the makeup rate exceeds 100 gal/h (378.5 L/h). With lesser quantities, the effects of the carbon dioxide generated can be controlled by the use of steam and return line treatments. The economics of using a dealkalizer can be determined by comparing the costs of the steam and return line treatments with the costs of installing and operating a dealkalizer.

In installations where the steam comes in direct contact with food products, the U.S. Food and Drug Administration permits use of certain treatments for control of carbonic acid induced corrosion under limited conditions (21 CFR §173.310) When it is not possible to control the treatment within these specified limitations, installation of a dealkalizer would be justified to remove 90 percent of the alkalinity, to reduce the excessive corrosion tendencies of the steam and return condensate.

The dealkalizer contains an ion-exchange resin similar to the water softener with the capability of exchanging carbonate, bicarbonate, sulfate, and other anions for chloride, hence the name "chloride anion dealkalizer"

The dealkalizer installed must be sized to remove the alkalinity from the makeup water and to deliver dealkalized water at a rate of 6% gal/mm (25.2 L/min) per 100 bhp [3450 lb/h (1565 kg/h) steam rate] so that it would be able to deliver the maximum amount of makeup water required at any given moment of operation. It usually accompanies the ion-exchange water softener and is installed as a complete packaged softener-dealkalizer. With this equipment, alkalinity is reduced and corrosion of steam and return condensate lines can be controlled.

6.3 Deaerators

To prevent serious corrosion and pitting of steam boiler feedwater lines and boiler tubes, it is necessary to remove the dissolved oxygen from the boiler feedwater, which may be done by the use of chemical treatment.



In many installations, however, it is neither practical nor economical to use chemical treatment alone. In these circumstances, it is necessary to remove most of the dissolved oxygen mechanically by using feedwater heaters or deaerators followed by small quantities of treatment to remove the last traces of corrosive gases.

Whenever a steam boiler system is open to the atmosphere through vented condensate receivers, feedwater tanks, etc., the air absorbed will result in high quantifies of dissolved oxygen. This increases in direct proportion to the amount of makeup water used because the cold raw makeup water, high in dissolved oxygen, not only will increase the dissolved oxygen content, but also will lower the temperature of the feedwater in the return condensate tank, enabling more oxygen from the atmosphere to be dissolved in the feedwater. This happens because the solubility of oxygen in water is inversely proportional to temperature. Figure 6.1 shows the solubility of oxygen with respect to temperature.

The feedwater temperature of low-pressure heating boilers operating with theoretically all return condensate will remain close to 180 to 200°F (82 to 93°C) since little or no cold-water makeup is used. In systems such as this, a deaerator or feedwater heater is not usually required. Hence the current design custom is to avoid the use of preheaters or deaerators with low-pressure heating boilers. However, if the low-pressure steam heating boiler were to operate with any steam loss such as at steam humidifiers in air-handling units or steam tables or pressure cookers in a cafeteria or restaurant, the cold-water makeup replacing that loss increases the dissolved oxygen content. In these cases it is essential that a mechanical preheater or deaerator be used to remove the dissolved oxygen from the feedwater Without it, the cost for chemical oxygen scavengers alone is excessive.

The simplest mechanical deaerator is the open feed-water heater or preheater. This consists of open or closed steam coils placed in the vented condensate tank. The coils are thermostatically controlled to maintain the temperature of the feed water at 180 to 200°F (80 to 95°C) or the highest possible temperature without causing boiler feed-water pump difficulties such as cavitation or steam shock.

The deaerator is a more complex device that utilizes steam injection to scrub the incoming makeup water and condensate of the dissolved corrosive gases, oxygen and carbon dioxide. In the deaerator, water is sprayed over inert packing such as glass beads or plastic fill or is trickled through baffles or trays to break up the water and provide for intimate fixing of the feed water with the incoming steam. The steam is injected counter to the flow of the incoming water, which drives the gases, oxygen and carbon dioxide, upward out the vent. The vent releases only noncondensible gases and steam losses are at a minimum.

Some deaerators can produce a feed water with dissolved oxygen content as low as 0.005 cm³/L. To completely protect the equipment, the last trace of oxygen must be removed by superimposing a chemical oxygen scavenger, also packaged deaerating heaters can provide a feed-water quality of 0.03 cm³/L dissolved oxygen that is more than adequate for HVAC boiler systems. These packages include a factory- assembled unit complete with deaerating heater, controls, boiler feed-water pumps, and level controls. The deaerating heater consists of a storage or collection tank for condensate and raw makeup water and the deaerator section. The feed water is pumped from the storage section through a spray manifold into the top of the deaerating section. Steam is injected through a sparge pipe into the bottom of the deaerating section and is bubbled through the feed water. The steam drives out the oxygen and carbon dioxide gases through the vent.

Ideally, mechanical equipment should be employed to remove dissolved corrosive gases from boiler feed water for both low- and high-pressure boilers (in addition to chemical treatments). Similarly, to reduce corrosion risks, cold-water makeup should, ideally, be pre-heated.

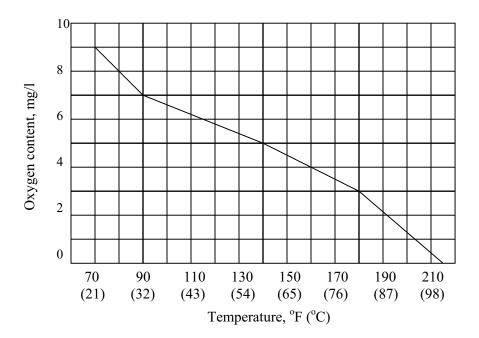


FIGURE 6.1 Solubility of oxygen from air at atmospheric pressure

6.4 Abrasive Separators

In closed hot water circuit, dual-temperature chilled/hot water circuit, or, so-called, secondary recirculating water systems, one of the major problems is the presence of suspended matter. Suspended matter not only causes deposit corrosion and fouling of heat-transfer surfaces, but also can seriously damage mechanical seals and shafts on pumps. Hard and abrasive particles will score shafts and mechanical seals, causing leaks and premature failures.

Mechanical seal failures are frequently attributed to the water treatment used in the recirculating water when they are actually caused by abrasives, finely divided iron particles, grit, sand, and other foreign particles. Water treatment and other minerals dissolved in the water will not cause seal failures unless excessive operating temperatures are encountered. This causes flashing of the water lubricant at the seal interface, resulting in precipitation of dissolved minerals which end up scoring the seal surface in the absence of the water lubricant. This occurs at temperatures in excess of 160°F (71°C).

To minimize these failures, very inexpensive abrasives separators are used. These not only remove the suspended abrasive particles from the water lubricant at the seal interface, but also force clean, clear water at the pump discharge pressure back into the seal cavity, preventing flashing due to excessive temperatures.

A typical abrasives separator device removes suspended abrasive particles by centrifugal force as the water piped from the pump discharge enters the separator and is rotated in the cone-shaped bore at a high velocity developed by the pressure differential. Clear water is taken from the middle of the top outlet and piped to the pump housing for flushing the seal faces. This clear flush water under pump discharge pressure prevents flashing at the seal surfaces.

In larger installations, magnetic separators may additionally be installed.



6.5 Strainers and Filters

It is common practice to install strainers prior to pumps on open recirculating condenser water systems to protect the pump internals, vanes, shaft and impellers from large damaging flakes of rust, suspended dirt, or other foreign particles that can enter an open system. Similarly, strainers should be installed on closed systems since they are frequently plagued with suspended black magnetic iron oxide mill scale as well as foreign particles.

The bucket strainer can be used as a coarse filter to remove larger particles before the pumps and heat exchangers. Iron and steel particles, however, can be so small that they pass through the finest mesh screen. Magnetic inserts attached to the strainer's bucket catch the fine iron particles, which can then be cleaned out by flushing with a high-pressure hose.

6.6 Free Cooling

One of the most interesting applications of strainers and/or filters on open cooling tower water systems is described in U.S. Patent 3,995,443 dated December 5, 1976. This patent describes a process commonly called "free cooling" or "crossover cooling." During seasons of the year when the cooling tower water temperature can be held at 60°F (15.5°C) or below, the tower water is diverted to the chilled- water circuit bypassing the refrigeration machine. In this way, cooling is provided by naturally cool cooling tower water rather than by artificially chilled water. This procedure can provide substantial savings in energy since the refrigeration machine does not have to operate during the off-peak spring and fall months in certain areas of the Country.

The dangers of diverting cooling tower water to the chilled-water circuit are obvious. Suspended matter, airborne particles, dirt foulants, mud, slime, etc., commonly present in open cooling tower waters can seriously foul chilled-water circuits. These systems have much narrower passageways in fan-coil units, terminal units, air-handling units, etc., with delicate controls, often needle valves, which are readily fouled by even the slightest amount of suspended matter. Therefore, it is necessary to maintain the cooling tower water free of suspended matter and foulants if such a procedure is to be successfully applied.

Methods of keeping the system clean include use of modem polymeric dispersants and deposit inhibitors along with very fine separators, strainers, bag, sand or multimedia filters. The use of highly efficient heat exchanger in place of strainers frequently solves the contamination problem by isolating the closed circuit from the open circuit in "free- cooling" systems.

6.7 Non-Chemical Treatments (Magnetic, Electrostatic and Similar Devices) and "Gadgets"

From time to time over the past 50 years or more, various forms of non-chemical devices and gadgets have appeared for which exaggerated claims have often been made. All are said to eliminate and prevent all forms of deposits in recirculating water systems and boilers without the use of chemical treatment. Some claim to also control corrosion, and others biological fouling. Some of these technologies are summarized below:

Magnetic devices. A magnet(s) is fixed onto, or plumbed into a system, along the parallel axis of water flowing in a pipe. It is claimed, that with careful sizing and fitting, these devices inhibit the formation of scale.



Electrolytic devices. These devices consisting essentially of a *zinc anode* and a *copper cathode*, are plumbed in a system and in contact with the water (electrolyte); they are claimed to prevent scale by acting in a similar way to a battery.

Electrostatic devices. These devices provide a "static field within the water" via the production of a very high, localized voltage (but low current). It is claimed that this field physically affects the dissolved mineral ions and inhibits the precipitation of scale.

Electronic devices. There are various designs, including square-wave generators, sonar effect and frequency modulation (FM) devices. The signal generated is typically applied to a closed-coil, formed by wrapping a signal cable around the outside of a water pipe. These devices are claimed to transfer energy to the ions of dissolved bicarbonate minerals, creating nanocrystals and preventing scaling of metal surfaces and holding the minerals in suspension until they can be bled from the system.

Catalytic devices. These non-magnetic devices use a perforated non-ferrous tube to encourage small calcite seed crystals to form and reduce the risk of bulk water scaling. They are promoted for use in hard waters under conditions where supersaturation can easily occur.

Pressure-changing devices. In these devices, it is claimed that when water flows through a perforated bar or tube, the pressure drops drastically, causing dissolved *carbon dioxide* to escape, raising the pH slightly and resulting in the water being supersaturated with millions of tiny calcite (crystalline *calcium carbonate*). These grow to sub-colloidal size and are eventually dislodged into the bulk water by the shearing force of the water flow and remain suspended as discreet particles, rather than agglomerating as scale.

Many of these devices are rightly called "gadgets" and simply do not work. Others may have some limited effect on controlling scale, but even when seed crystals, nanocrystals or sludge is produced, unless this material is regularly removed from the water system, deposition, fouling and loss of heat-exchange will still occur. None of the devices have any practical control over corrosion or biological fouling. For many buyers or operators of building and similar HVAC type water systems, the allure of non-chemical devices is very appealing, however such appeal may be significantly outweighed by the, often very high, equipment capital purchase or leasing costs.



7. TREATMENT OF BOILERS

7.1 General

The chemicals, equipment, and method of treatment required to optimize water treatment systems to reduce the corrosion, scaling, and fouling to accepted minimums must be tailored not only to each system but also to each geographic location.

To obtain the optimum treatment of each system, it is strongly recommended that a reputable water treatment company and/or water treatment consultant be retained to select the chemicals, equipment, and method of treatment for each system required and to provide effective monitoring, control and review services.

7.2 Treatment of Boiler Water Systems

General. Internal treatment of HVAC boilers is required to prevent the problems of corrosion, pitting, scale deposits, and erratic boiler operation due to priming, foaming, and carryover. To prevent these problems, correct blowdown and treatment must be applied.

Blowdown. Blowdown of a boiler is the spontaneous removal of some concentrated boiler water from the boiler under pressure. The recommended maximum concentrations of these impurities, which must be properly controlled, are outlined in table 7.1. These limits are for boilers with an operating pressure up to 250 psig (1724 kPa) and are used as a guide only. Actual operating experience will determine the true limits with any specific boiler operation.

The number of times that the solids in the makeup water have been accumulated in the boiler water is called the "cycles of concentration." To determine the required amount of blowdown, it is necessary to examine the makeup water analysis and compare it to the maximum allowable concentration of solids as outlined in table 7.1.

The maximum cycles of concentration permitted for each of the items listed in the table is determined by dividing the maximum values in this table by the amount of each given in the makeup water analysis.

Let us examine the water analysis of Omaha, NE (figure 8.1), and compare it with the maximum concentration of solids allowed in a boiler (table 7.1), to determine the maximum cycles of concentration allowed:

TABLE 7.1 Maximum Concentration of Boiler Water Solids for Boilers receiving Feedwater with Hardness of < 2.0 ppm and Operating at Pressures up to 300 psig (314.7 psia, 21.7 Bar, $2170 \text{ kPa}, 2170 \text{ kN/m}^2$

Silica	150 mg/L as SiO ₂
Suspended solids	200 mg/L
Total dissolved solids	3500 mg/L
Total alkalinity	1000 mg/L as CaCO ₃





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CERTIFICATE OF ANALYSIS - VARIOUS WATER ANALYSES

LOCATION	1	2	3	4	5	6
PARAMETER						
рН	9.2	7.9	7.0-10.0	11.3	10.5-11.5	7.5
P ALKALINITY, as CaCO ₃ mg/l	10	0		153	200-400	
BICARBONATES, as CaCO₃mg/l	52	250				167
CARBONATES, as CaCO₃ mg/l	20			122		
HYDROXIDES, as CaCO ₃ mg/l				92		
M (TOTAL) ALKALINITY, as CaCO ₃ mg/l	72	250		214		167
TOTAL HARDNESS, as CaCO ₃ mg/l	159	86		0		149
SULFATE, as SO ₄ mg/l	181					
SILICA, as SiO ₂ mg/l	7.7			23		10
IRON, as Fe mg/l						
CHLORIDE, as NaCl mg/l	23	35		841		187
SPECIFIC CONDUCTANCE microS/cm	415	3831		2244		815
TOTAL DISSOLVED SOLIDS mg/l		3448		1818	3000 max	501
MOLYBDATE, as Na₂MoO₄ mg/l		460	400-600			
PHOSPHATE, as PO ₄ mg/l				50	30-50	
SULFITE, as Na ₂ SO ₃				35	30-50	

1 = Omaha, NE: Florence Plant

2 = Sample from LP steam boiler

3 =Controls/recommendations for LP steam boiler

4 = Sample from HP steam boiler

5 =Controls/recommendations for HP steam boiler

6= Harrisburg, PA: City water

FIGURE 7.1 City Waters and Boiler Water samples



<u>Analytical results</u> <u>Maximum cycles of concentration</u>

Silica, mg/L:

 $\frac{\text{Maximum}}{\text{Makeup water}} = \frac{150 \text{ mg/L}}{7.7 \text{ mg/L}} = 19.5x$

Suspended solids (hardness), mg/L:

 $\frac{\text{Maximum}}{\text{Makeup water}} = \frac{600 \text{ mg/L}}{159 \text{ rng/L}} = 3.8x$

Total dissolved solids, mg/L:

 $\frac{\text{Maximum}}{\text{Makeup water}} = \frac{3000 \text{ mg/L}}{415 \text{ mg/L}} = 7.2x$

From the above we see that the maximum allowable cycles of concentration are 3.8x. The lowest value obtained is used, for if this value were exceeded, difficulty with that particular impurity would result. If the makeup water were softened, hardness would be removed and no longer considered a limiting factor. In this case, the maximum allowable cycles of concentration would then be increased to 7.2x, the next lowest value. In practice, a water softener would be essential.

After the maximum allowable cycles of concentration in a boiler are ascertained, the blowdown rate required to maintain the solids accumulation below this maximum level can be calculated. Blowdown is used to remove accumulated boiler water solids.

The amount of solids present in the concentrated boiler blowdown water is equal to the amount of solids in the makeup water multiplied by the cycles of concentration. This can be expressed mathematically as *BCX*, where:

B = blowdown, gal(L)

C = cycles of concentration

X = total solids concentration of makeup water, ppm (mg/L or g/gal)

The amount of solids entering the boiler with the makeup is expressed mathematically as MX, where:

M = makeup water, gal (L)

Since blowdown is designed to maintain a specific level of cycles of concentration, that level can be kept consistent only if the amount of solids leaving the boiler is precisely equal to the amount of solids entering the boiler. This is expressed mathematically as:

BCX = MX(solids leaving) (solids entering)

Solving this mathematical equation for blowdown *B*, we obtain:

 $B = \underline{\underline{M}}$



This formula is used to determine a blowdown rate with respect to the makeup rate. In percent, it can be expressed as:

% Blowdown =
$$\frac{100}{C}$$

In actual practice, however, it is not usually possible to measure the blowdown rate even though it is possible to calculate the amount required. Therefore, to determine if the blowdown rate is sufficient, the cycles of concentration are measured through the use of a simple chloride test.

Chlorides are the most soluble minerals and are always present in the makeup water in some degree. In addition, chlorides are only added to a boiler with the makeup water and not with treatment or from any other source. The cycles of concentration are found by comparing the chlorides of the makeup water with the chlorides of the boiler water:

This very simple and practical test is used by operating engineers to control the blowdown rate.

7.3 Internal Treatment of Boiler Water Systems

Scale and Sludge Control After the maximum allowable cycles of concentration are determined and a blowdown rate is established to prevent accumulation of minerals beyond the maximum allowable limit, treatment to prevent deposits and maintain precipitated solids in suspension must be considered. As outlined previously, the hardness minerals, calcium and magnesium, are precipitated in the boiler water and tend to build a scale on the heat-transfer surfaces unless some treatment is used. Without treatment, these minerals will eventually precipitate as the insoluble carbonate and sulfate salts.

Similarly, silica and complex silicates will form hard, dense scales if silica is present in excess of its solubility. Some treatment for preventing these hard, dense scales includes phosphate to preferentially precipitate the calcium as phosphate, and in the presence of excess alkalinity phosphate is precipitated as calcium hydroxy-phosphate, also known as hydroxyapatite [Ca₃(PO₄)₂· Ca(OH)₂]. Magnesium with hydroxide alkalinity present in the boiler water will form the hydroxide precipitating as brucite (MgOH₂). In these forms, the particles are more easily dispersed and held in suspension.

Non-phosphate treatments may consist of carbonate and silicate salts to preferentially precipitate calcium carbonate and magnesium silicate, which are more readily dispersed and held in suspension by polymers. The formulated boiler water treatment may include soluble organic polymers such as lignins, tannins, and polyelectrolytes that promote formation of the insoluble precipitate within the boiler water rather than on the heat-transfer surface. These materials act as nucleating sites, or places for the soluble ions to meet and form the insoluble particle dispersed throughout the boiler water. Some polymers are called "polyelectrolytes" because of their many positive and negative electrolyte sites on the polymer chain.

The polyelectrolytes such as polyacrylamides, polyacrylates, polymethacrylates, polymerized phosphonates, polymaleates, and polystyrene sulfonates also distort the crystal growth of the scale particle, rendering it less adhesive to heat-transfer surfaces and more readily dispersed with reduced tendency to compact into a dense scale.



Some modern polymers also sequester hardness similar to the chelates, and additionally act to redissolve existing deposits. These polymers, therefore, act to prevent and remove scale by a threefold mechanism of dispersion, crystal distortion, and sequestration.

Another type of scale inhibitor is the chelating agent. Chelants are organic materials capable of solubilizing calcium, magnesium, and iron, preventing formation of the insoluble salts. Both EDTA (ethylenediaminetetraacetic acid) and NTA (nitrilotriacetic acid) are used in boiler water treatment as chelates to prevent scale formation and in some cases to remove existing scale deposits. The use of these materials in HVAC equipment is limited because they require close control and are particularly corrosive to iron when they are not controlled. Some proprietary formulations contain small amounts of chelants to provide very efficient scale control. Combinations of chelating agents and polymers have been widely applied with excellent results.

Boiler Section Corrosion Control by Alkaline Treatments. Corrosion in boilers may be controlled with oxygen scavengers, alkalinity boosters and corrosion inhibitors. Corrosion of iron is greatly influenced by the pH value of the water in contact with the iron. The lower the pH value, the higher the corrosion rate; and the higher the pH value, the lower the corrosion rate.

At a pH of 11.0, the corrosion rate of iron will be virtually nil, provided oxygen and other corrosive gases are removed. Treatment of boiler water to control general corrosion, therefore, will include an alkaline substance to raise the pH value to 10.5 to 11.5. This range is compatible with normal operation without foaming or carryover, and at the same time, it will promote good corrosion control.

The alkaline materials include potassium and sodium hydroxide (commonly called caustic potash and caustic soda respectively) and sodium carbonate commonly called soda ash.

Boiler Section Corrosion Control by Oxygen Removal. As we have seen, dissolved oxygen in boiler water causes localized corrosion called pitting, and to prevent pitting, the oxygen must be removed. This is another way to alter or stabilize the environment. Deaerators are used for this purpose, but no deaerator is perfect, and the best ones produce a boiler feed water with a dissolved oxygen content of 0.005 cm³/L. This very low oxygen content can cause serious pitting failures especially in boiler feed-water lines and at boiler tubes adjacent to the feed-water entrance to the boiler. To prevent this, chemical oxygen scavengers are used to absorb the oxygen from the water and to ensure a completely oxygen-free environment. The most common oxygen scavengers are sodium sulfite and hydrazine. These materials have a strong affinity for oxygen and will absorb it from the water.

Sodium sulfite is widely employed, and approximately 8 ppm is needed for every 1 ppm of oxygen. As a fairly high sulfite reserve is required (typically 20-50 ppm or more), additional sulfite must be added and so the general rule is 10 ppm of sodium sulfite per 1 ppm oxygen. The maintenance of a slight excess of the oxygen scavenger in the water provides assurance that there is no dissolved oxygen present. Complete water treatment formulations containing sodium sulfite for this purpose will also include a catalyst, ensuring that the reaction between the dissolved oxygen and the oxygen scavenger is instantaneous, even in cold water.

Hydrazine is not widely used as an oxygen scavenger due to its toxicity. Other oxygen scavengers currently used as a replacement for hydrazine include diethylhydroxylamine (DEHA), sodium erythorbate, carbohydrazide (CHZ), methylethylketoxime (MEKO) and hydroquinone (HQ). Typical reserves for these materials are very low, perhaps only 0.1-0.2 ppm.

Tannins are also used. They have been employed for over a century and have significant benefits over other oxygen scavengers in many HVAC situations, as, being organic, they do not contribute to TDS as when using sulfite, and they are much less expensive than DEHA or erythorbate.



The hydrolyzable tannin component of *Quebracho* and other tannins, under alkaline BW conditions produce a number of oxygen scavengers, primarily as the sodium salts, these include, tannic acid, ellagic acid, gallic acid, quinic acid, pyrogallol, hydroquinone and catechol. In addition, they are very good passivators and reasonable sludge dispersants.

Tannins do impart a brown color to the boiler water, which can sometimes make testing for hardness, chlorides or alkalinity a little difficult when looking for subtler color changes, but the mere presence of a strong brown color confirms its presence and provides reassurance that oxygen corrosion is under control.

Boiler Section Corrosion Control by Passivating Agents. Corrosion inhibitors are substances which do not necessarily alter the environment, or conditions involving the corrosion process, but act as a barrier between the corrosive medium and corroding metal surface, Physical barriers such as protective coatings and galvanizing immediately come to mind as a common application of a corrosion inhibitor. These physical bathers actually separate the corrosive atmosphere containing water, oxygen, and acid gases from the base metal.

Corrosion inhibitors can be added to water which form a protective film on the metal surface, acting as a barrier to the corrosion process, i.e., inhibiting the corrosion reaction. Such barriers form by a chemical reaction between the metal surface and the inhibitor or by a physical attraction and adsorption on the metal surface. With this type of inhibitor, the film is not visible and nonaccumulative. The thickness is only the thickness of one molecule of the inhibiting film, hence, it is called a "monomolecular film." With a film of this thickness, there is no interference with heat transfer, and therefore the inhibitors are found to be very effective in heat-transfer equipment. The films formed can be either adsorbed films, as in some organic inhibitors, or a chemically formed reaction product of the inhibitor and metal surface. The inhibiting film may also be a combination of both adsorption and reaction. The result is a reduction of the corrosion rate and passivity.

Passivity is described as a state of an active metal in which reactivity is substantially reduced, resisting corrosion, or when its electrochemical behavior becomes that of a less active metal. That is, the metal becomes passive or is passivated. Inhibitors in this sense are also called "passivators." Inorganic inhibitors used in boilers for this purpose are molybdates, nitrites, borates, silicates, and phosphates. Some organic inhibitors used are phosphonates, polyacrylates, phosphinocarboxylic acids, and nitrogen-containing organics such as triazoles and amines.

Tannins are particularly useful as passivators and undergo a chemico-physical reaction at the boiler metal/water interface, forming an iron-tannate passivated (corrosion-inhibiting) film.

Post-Boiler Section Corrosion Control. Soda ash, although still sometimes used for pH control in boilers, is not desirable for HVAC boiler equipment. The carbonates added to boiler water, although they increase the boiler water pH, will decompose forming carbon dioxide gas which is a cause of corrosion of steam and condensate lines and heaters. The carbon dioxide dissolves in the steam condensate forming carbonic acid. This is very corrosive to steel and copper and can be a cause of failure of unit heaters and condensate handling lines and equipment. Even where carbonates are not added, natural bicarbonates and carbonates enter the boiler system in the makeup water and the same problems of carbon dioxide corrosion can develop.

The carbon dioxide generated from the carbonates and bicarbonates naturally present in the boiler makeup water can be neutralized by using neutralizing amines, mild alkaline materials related to ammonia but much milder than it. Amines used for this purpose are morpholine, cyclohexylamine, and diethylaminoethanol. These materials, liquid at room temperature, boil and vaporize at approximately the same temperature as water, thereby going off with the steam, a mixture known as an "azeotrope."



As the steam condenses into water, the amines also condense, rendering that initial condensate alkaline and much less corrosive to the metal surface. The flowing condensate containing the neutralizing amine will then retain higher pH values, even with the adsorption of carbon dioxide gases. For the flowing condensate, a pH range of 7.0 to 9.0 is the most favorable for good corrosion control of all metals in heating systems including iron, steel, brass, and copper.

In addition to the use of neutralizers in steam and return condensate lines, film-forming inhibitors are also used. These are organic amines or amides such as octadecylamine and mixtures of octadecanol and stearamide. These inhibitors form insoluble films on the seam and condensate piping. They will steam distill from the boiler; i.e., they carry over with the steam and deposit in the steam and condensate system. The disadvantage of such inhibitors is that this film is not self-limiting, and heavy deposits plugging steam traps, strainers, etc., can result unless particular care is taken to avoid this problem. The filming- type steam and condensate line corrosion inhibitors are employed most successfully in systems where there is little or no return condensate. In heating boilers where most condensate is returned, the neutralizing amines are more suitable. Combinations of neutralizing and filming amines are also used.

7.4 Summary of Boiler Water Treatment Chemical Functions

- Corrosion control This typically requires a combined approach that includes oxygen scavenging, maintenance of passivated films, and pH and alkalinity control. Sometimes, certain additional conjunctional treatments are required, such as **sodium nitrate** for protection against embrittlement
- Scale and deposit control primarily hardness salts and other scale forming minerals
- Sludge control includes control over a variety of foulants
- Carryover control foam, priming (surging), misting and process contaminants
- Specific contaminant control: including silica, iron, copper, sodium, chloride, caustic
- Steam/condensate line corrosion control oxygen, carbonic acid, and ammonia

Control over problems such as the supersaturation of dissolved solids, short and long-term overheating, and boiler priming (surging), rely at least as much on good operation.

7.5 Summary of Types of Internal Treatment Program Commonly Employed

Internal treatments for BW are chemical formulations having potentially beneficial single-, dual- or multifunctional effects. Globally, there are thousands of formulations available, and, for the most part, they can each be loosely classified as described below.

- **Anodic inhibitor programs:** These employ *nitrite, silicate* or *molybdate* chemistries for light-duty multifunctional programs in HW heating and LP steam boiler systems
- **Tannin programs:** These use blends of certain natural or synthetic tannins and provide oxygen scavenging, passivating and sludge conditioning functions



- Coagulation and precipitation programs: These are widely used and employ various types of phosphates as a precipitant to provide control over the unwelcome deposition of hardness scales. *Carbonates* and *polysilicates* were once commonly used
- **Chelant programs:** These are commonly prescribed for both FT and WT boilers either as replacements for, or used in combination with, phosphate precipitation programs
- All-polymer/All-organic programs: Many specialty polymers are now available and widely used in every type and size of boiler. Typically, multifunctional blends are used as phosphate replacements, to act as sludge conditioners, and to provide control over specific problems such as iron transport that can affect many boiler plant facilities
- Chelant, phosphate or polymer based, dual or multifunctional programs: Many permutations of dual- or multifunctional programs exist, based on either chelant or phosphate, together with polymers and related organics are widely employed
- Coordinated phosphate programs: These avoid the formation of hydroxyl alkalinity (free caustic) in higher-pressure WT boilers and require very careful control. Variants include congruent control and equilibrium phosphate treatment
- **All-volatile programs (AVPs):** These are employed in higher-pressure boilers (generally power boilers) and utilize only volatile chemicals, such as ammonia, amines (such as *diethylhydroxylamine*, DEHA), and other *vapor phase inhibitors* (VPIs)

In addition, certain primary and secondary functional chemicals (adjuncts), such as outlined below, are generally also required providing a comprehensive program.

- **Primary support chemicals** encompass *oxygen scavengers* and *condensate treatments*. Oxygen scavengers include *inorganics* such as sodium sulfite and *organics* such as hydrazine. Condensate treatments include *neutralizing amines* such as morpholine and *filming amines* such as octadecylamine (ODA)
- Adjuncts include *antifoams/defoamers* (generally polyethoxlyates), *problem-specific polymers* (typically for iron transport and silica control) and *alkalinity boosters*.

7.6 Control Measures and Additional Boiler Water Treatment Measures

Priming, Foaming, and Carryover. Priming of boiler water is the bumping and bouncing of the water level of the boiler during operation. Foaming, however, is a less violent activity. It consists of the formation of small bubbles in the surface of the boiling water like the soap foam in a washer. Carryover essentially is the contamination of the steam with boiler water. It is a result of priming and foaming and can be a more subtle entrapment of boiler water with the steam, causing steam contamination without the evidence of priming and/or foaming.

The causes of priming, foaming, and carryover can be many and varied. Most frequently, they are caused by contamination of the boiler water with oil or other foreign substances. Other causes are excessive solids accumulation due to the lack of blowdown, high alkalinity, overtreatment, or mechanical malfunction.



Adequate blowdown and certain antifoam treatments can reduce the problems of priming, foaming, and carryover.

Treatment of Low-Pressure Steam Heating Boilers. Most low-pressure steam heating boilers have a unique type of operation in that *all* the steam produced is for heating purposes *only*. Therefore, little makeup water is required as well as little accumulation of solids. The only makeup water is for slight loss at vents, leaks, or overflow at condensate receivers.

Without makeup water and accumulation of minerals, even with a very hard water supply, problems of scale formation are significantly reduced. However, corrosion under these conditions can become aggravated. The treatment program will usually consist of a corrosion inhibitor for the boiler and neutralizing or filming amine for the steam and condensate system.

This program, however, is limited to "closed" systems where all steam is returned to the boilers as condensate and where *no* steam is used for humidification or cooking, as in cafeterias or restaurants. Whenever steam is consumed, makeup water will tend to accumulate minerals in the boiler, and other treatment programs will have to be used, as described below.

The corrosion inhibitors most widely used in low-pressure steam boilers are sodium molybdate and sodium nitrite. To be certain that these inhibitors provide a continuous protective film and that no area of the metallic surfaces remains exposed certain minimum levels must be maintained. Inhibitors are required to provide buffering, so that the pH can be maintained at 7.0 to 10.0 for maximum effectiveness.

For treating the steam and condensate of low-pressure heating systems, the neutralizing amines can be added gradually at regular intervals in sufficient quantity to maintain the pH value of the condensate at 7.5 to 8.5. The neutralizing amines should not be used in systems containing nitrites or where steam is used for humidification.

Treatment of High- and Low-Pressure Process-Steam Boilers. Because high-pressure steam systems operate at higher boiler water temperatures than low- pressure steam heating boilers, they cannot be treated with the corrosion inhibitors mentioned above. The method of treatment of high-pressure steam boilers involves heat-stable substances such as environmental stabilizers that alter the condition responsible for corrosion and deposits.

With low-pressure steam boilers operating with some makeup water due to steam losses at steam humidifiers, kitchen steam tables, dishwashers, or for any other purpose, the conditions favoring use of corrosion inhibitors are altered. With makeup water required because of steam losses, minerals present in the makeup will tend to accumulate. This requires increased blowdown to reduce the mineral buildup and additional treatment to replace that lost in blowdown. Likewise, a different type of treatment including scale inhibitors will be required to prevent hardness in the makeup water from forming scale. Therefore, such systems must be treated as high-pressure steam boilers with environmental stabilizers, rather than with corrosion inhibitors.

Treatment for corrosion control will consist of adjustment of the alkalinity and pH value with caustic soda to maintain the pH value at 10.5 to 11.5 consistent with efficient operating conditions. The boiler feed water should be deaerated to remove dissolved oxygen and to prevent oxygen pitting, followed by superimposing of an oxygen scavenger to remove the last traces of dissolved oxygen. Materials used for this purpose are sodium sulfite at levels of 20 to 50 mg/L or the organic materials diethylhydroxylamine and sodium erythorbate.

In most HVAC applications, sodium sulfite is preferred because of cost and ease of storage, handling, and control. Organic materials are preferred when dissolved solids are objectionable, such as in electrode boilers. These do not add to the mineral content of the boiler water. Diethylhydroxylamine, however, has the disadvantage of forming ammonia or amines, which are corrosive to copper, brass, and other copper alloys commonly used in heating systems.



The choice of oxygen scavengers, therefore, must be carefully considered.

For control of scale and deposits, boiler water treatment includes a zeolite softener on makeup water when required, followed by internal treatment with phosphates, chelating agents, polymers, and/or dispersants. The basic program includes a phosphate polymer combination used to maintain a sodium phosphate concentration in the boiler water at 20 to 60 mg/L, ensuring that all the calcium has precipitated as phosphate.

The non-phosphate program includes polymers, phosphonates, or combinations of polymers, phosphonates, and chelants with the polymer in the range of 2 to 100 mg/L, depending on the type of polymer and formulation used. Chelates should not be used in excess of 2 to 3 mg/L free chelate because corrosion of iron can be accelerated in the boiler water.

Antifoam agents are used in the boiler water treatment formulations to prevent foaming and carryover. They enhance more efficient nucleate boiling and prevent foaming and carryover. Antifoam agents for boilers include polyalkalyene glycols and polyamides used at 10 to 100 mg/L. Finally, the treatment program for high-pressure steam boilers and low-pressure process boilers should include a steam and return condensate line corrosion inhibitor. This should be either a neutralizing amine or a mixture of neutralizing amines to maintain the pH of the condensate at 7.0 to 9.0. Where the steam loss is high and the use of neutralizing amines is too costly, a film-forming inhibitor may be used to protect the condensate piping.

7.7 Feed and Control of Boiler Water Treatment Programs

Test Controls. The test control of water treatment is one of the most important aspects of the water treatment program. Without proper testing, more harm than good can result.

A typical analysis of a low-pressure steam boiler using a sodium molybdate inhibitor is shown in figure 7.1. With high-pressure steam boilers and low-pressure process boilers, the tests must be made more frequently. Testing 3 times a day may be required if load variations are such that conditions can change that rapidly. Daily testing with field test kits is more common and the preferred frequency for best results.

A typical test analysis of a high-pressure steam boiler water, with recommended controls, is also shown in figure 7.1. Field test kits are available for easy testing of boiler water samples, these test kits range from simple drop tests for chloride and sulfite, etc. to burettes, to colorimeters and even laboratory spectrophotometers. More elaborate test cabinets are generally used in large boiler room where a watch engineer is on duty to make tests at frequent intervals.

Feed Methods. Water treatment is applied to boilers by various means, ranging from shock dosage to highly sophisticated chemical proportioning pumps and controllers. These methods are briefly described:

Shock Feed Methods. Shock feeders are most convenient and effective with low-pressure heating boilers, which require only periodic addition of a corrosion inhibitor and perhaps weekly addition of a steam condensate neutralizing amine. One of the handier devices for this purpose is the force hand pump which adds treatment directly to the boiler through a ¾-in (20-mm) drain cock..

Another shock device is the pot type or bypass feeder. This kind of feeder should be installed on the makeup water line to the boiler to inject treatment directly into the boiler with the pressure of the boiler feedwater pump. If it is installed on a raw makeup water line, an approved backflow preventer must be used to avoid the possibility of raw water contamination with boiler water treatment.



Proportioning Feed Methods. With high-pressure steam boilers and low- pressure process boilers, it is desirable to feed treatment to other boiler continuously in proportion to actual need. Proportioning feed systems will feed treatment based on feedwater flow.

Basic Proportioning Feed System. A simple proportioning feed system consists of a chemical feed pump interlocked with the boiler feedwater pump to transfer treatment directly from the drum into the feedwater tank prior to the boiler. This method is ideal where a single liquid boiler treatment formulation is used that contains all the required corrosion and deposit inhibitors without phosphates.

Proportioning Water Treatment System for Steam Boilers without Deaerator This more complex program requires a more sophisticated feed system. The treatments with alkalinity and phosphates must be added directly to the boiler to prevent deposits in the feedwater line and damage to feedwater pumps.

Proportional Water Treatment System for Steam Boilers with Deaerators. When deaerators are installed, it is best to feed treatments for corrosion and pitting directly to the storage section of the deaerator. Some deaerator manufacturers warn against feed of treatment to the storage section of the deaerator if phosphates and other alkaline compounds are used, because they can cause precipitation of deposits prior to the boiler and can damage the deaerator tank, boiler feedwater pump, and lines. In this case, the phosphate and alkaline treatments should be fed directly to the boiler, and only the oxygen scavenger and amine, or other non-deposit-forming materials, should be fed into the preboiler section. When this is explained to the deaerator manufacturer, the objection is usually removed.

Automatic Blowdown and Feed Controllers. Since ASME (American Society of Mechanical Engineers) code restrictions prohibit installing automatic valves on the bottom blowdown line, use of controllers and automatic valves is restricted to the side or top continuous blowdown line. The side or top blowdown is strictly used for controlling dissolved solids, because it will not remove suspended solids settled in the bottom of the boiler. Even when top blowdown controllers are installed, the bottom blowdown still must be administered to remove the settled and suspended solids. The top blowdown must never be used as a substitute for the bottom blowdown.

8

THE METRO HANDBOOK OF WATER TREATMENT FOR HVAC SYSTEMS

TREATMENT OF OPEN RECIRCULATING WATER SYSTEMS

8.1 General

The major problems encountered in open cooling water systems are corrosion and deposits of scale, dirt, mud, and organic slime or algae growths. In open systems, there is a loss of water caused by both evaporation and windage drift. The water lost by drift will be of the same quality as the recirculating water; i.e. it will contain the same amount of dissolved minerals and impurities. The water lost by evaporation, however, will be of a different quality.

Evaporation from the recirculated water will be pure water vapor similar to water produced by distillation containing, theoretically, no minerals or dissolved solids unless droplets of water spray are carried over with the water vapor. This pure water vapor leaves the dissolved minerals behind in the recirculating water since they do not vaporize with the water. The water lost by evaporation is replaced by makeup water, which contains dissolved minerals and impurities. As a result, there is an accumulation of minerals that constantly increases as the water in the system makeup water is introduced. Eventually the recirculating water will become so saturated with minerals that the most insoluble salts will come out of solution and form a scale on heat-transfer surfaces or within other parts of the system. To avoid this, the mineral content of the recirculating water must be controlled and limited. This is done by bleed-off.

Bleed-off. Bleed-off is the continuous removal of a small quantity of water concentrated with minerals from an open recirculating cooling water system. The water lost by windage drift also contains concentrated minerals and can be considered as bleed-off water.

The term "zero bleed-off" refers to the most ideal situation where the windage drift is such that the minerals and suspended matter lost with the drift Water droplets are sufficient to eliminate any need for an additional continuous bleed-off. In most cases, however, an additional bleed-off is required to limit the solids accumulations.

The most troublesome mineral scale is calcium carbonate since it is the least soluble of the salts present in the recirculating water. Inhibitors are used to increase the solubility of calcium carbonate and some other minerals, but even when they are used, it is necessary to limit excessive concentration of minerals by bleed-off. Bleed-off also limits concentrations of alkalinity, total hardness, and silica.

Alkalinity should be limited to prevent precipitation of calcium carbonate scale. Alkalinity is present in the form of bicarbonates and carbonates which combine with calcium and magnesium to form calcium carbonate and magnesium carbonate. (Calcium carbonate, being less soluble than magnesium carbonate, will form first). Alkalinity should be limited not only to prevent precipitation of calcium carbonates, but also to prevent high pH conditions, which may be damaging to some system components such as galvanized steel, brass, or cooling tower lumber.

With a total alkalinity of 500 mg/L, the pH value of a cooling tower water is expected to be approximately 8.7-8.8. This is based on the average pH of cooling tower water (not treated with acid), as shown in Table 8.1. This chart shows the expected average actual pH value, which will vary according to atmospheric conditions, make up water alkalinity and cycles of concentration. With regard to atmospheric conditions, for example, if the atmosphere has a considerable quantity of carbon dioxide and/or sulfur dioxide, these gases will tend to neutralize the alkalinity of the cooling tower water. For this reason, the alkalinity of the cooling tower water is not always a mathematical total of alkalinity from the makeup water; therefore, the condition may vary from location to location, and the maximum limitation of 500-800 mg/L of alkalinity as calcium carbonate is used only as a guide.



White Rust. One of the most frequently occurring problems caused by high alkalinity is that of "White Rust." White Rust is the deposit of zinc corrosion product, zinc carbonate, ZnCO₃, and basic zinc carbonate, 3Zn(OH₂)·ZnCO₃·H₂O. These products accumulate as a white waxy-like substance on the surface of galvanized metal of cooling towers. White rust is a complex phenomenon caused by high alkalinity of the cooling tower water and highly reactive poorly passivated galvanized sheet metal as a result of changes in the galvanizing process in the mid 1980s. This problem can be controlled by cleaning and passivation of the zinc galvanized tower prior to starting up with a cleaner containing phosphate passivators. Treating with corrosion inhibitors containing phosphonate or phosphate and maintaining pH value of the tower water at 7.0 - 8.0 pH should follow this program.

Total hardness should be limited to prevent calcium sulfate scale. Sulfates are naturally present in the recirculating water or are added in the form of sulfuric acid for pH control.

When the concentration of calcium hardness exceeds the solubility of calcium sulfate, it will come out of solution. Inhibitors can be used to extend this solubility by forming a supersaturated solution. But bleed-off must still be used to maintain the maximum limit.

Where all the hardness salts are present as bicarbonate or carbonate, the limitation of total hardness as calcium carbonate is typically 400-600 mg/L. However, where sulfuric acid is employed or where sulfates (the next least soluble of the calcium salts) are naturally predominant (as in some well waters) the limit is somewhat higher.

If calcium sulfate exceeds 1200-1500 mg/L (calculated as calcium carbonate), it tends to precipitate, or, depending upon the water chemistry, a supersaturated solution may form. Scale inhibitors can extend this solubility beyond this natural maximum, perhaps up to 1.6x saturation, but the guideline of 1200 mg/L maximum is typically used to limit the cycles of concentration and control stress operating conditions.

Silica must be limited to prevent silica scale, and the limit is the solubility of silica at the temperatures encountered. The silica limitation is based on the solubility of silicon dioxide (SiO_2) at the temperatures encountered in HVAC cooling-water systems. Silica is typically soluble up to approximately 150 mg/L, beyond this concentration it will tend to come out of solution.

Other factors, such as presence of scale inhibitors, the presence of magnesium and other mineral salts, and the alkalinity of the water will also have an influence on this.

TABLE 8.1 Expected recirculating water pH values (\pm pH_{actual}), at various cycles of concentration (COC), using makeup water sources of varying initial total alkalinity (TA).

Recirculating	MU water	MU water	MU water	MU water	MU water
Water pH @	with 25 ppm	with 25 ppm	with 100 ppm	with 200 ppm	with 400 ppm
various COC	T. Alk	T. Alk	T. Alk	T. Alk	T. Alk
рН @ 2x	7.1	7.5	7.9	8.2	8.6
рН @ 3х	7.4	7.8	8.2	8.6	9.0
рН @ 4х	7.7	8.1	8.5	8.9	9.3
рН @ 5х	7.9	8.4	8.8	9.1	9.5
pH @ 6x	8.1	8.6	9.0	9.4	9.7
рН @ 7х	8.2	8.7	9.2	9.5	9.8
рН @ 8х	8.3	8.8	9.4	9.6	-
рН @ 9х	8.4	8.9	9.5	-	-
pH @10x	8.5	9.0	-	-	-



Where silica is a factor, this limitation is typically used as a guide in determining the maximum cycles of concentration permissible.

The maximum concentration levels of alkalinity hardness and silica that are suggested with scale inhibitors present are shown in table 8.2.

Once the maximum limitations for certain dissolved minerals permitted in a recirculating cooling water system have been established, it is necessary to limit these minerals by bleed-off. The maximum cycles of concentration recommended for each of the items listed in table 8.2 are determined by dividing the maximum values in this table by the amount of each found in the makeup water analysis. To demonstrate how this is done, let us examine a city water analysis from Harrisburg, PA (figure 7.1), and determine the maximum cycles of concentration to be recommended in a cooling tower system water.

Shown below is a comparison of each of the limiting impurities with that impurity in the makeup water, to determine the maximum cycles of concentration.

<u>Analytical results</u>			Maximum cycles of concentration			
Alkalinity Maximum Makeup water	=	500 mg/L 167 mgJL	=	3.0 <i>x</i>		
<i>Hardness</i> <u>Maximum</u> Makeup water	=	1200 mg/L 149 mg/L	=	8.0 <i>x</i>		
<i>Silica</i> <u>Maximum</u> Makeup water	=	150 mg/L 10 mg/L	=	15.0 <i>x</i>		

From this table we see that the maximum cycles of concentration recommended are 3.0x. The lowest value obtained is used, for if it were exceeded, difficulty with that particular impurity would result. In this case, it would be the alkalinity, an excess causing precipitation of carbonate salts or excessive pH conditions. If a neutralizing acid were used in a system with this water, the alkalinity would be reduced and no longer considered a limiting factor. In that case, the maximum cycles of concentration would be increased to 8.0, the next lowest value.

TABLE 8.2 Maximum Concentration of Mineral Solids for Chemically Treated Cooling Water employing Evaporative Condensers and Cooling Towers

Mineral Solids	Evaporative Condensers	Cooling Towers
Silica	120 mg/L	150 mg/L as SiO ₂
Total alkalinity	500 mg/L	800 mg/L as CaCO ₃
Total hardness	800 mg/L	1200 mg/L as CaCO ₃

Note: Air Washers, Spray Coils, etc. are not normally comprehensively chemically treated and cannot operate at the maximum levels indicated above



After the maximum cycles of concentration recommended in an open recirculating cooling water system have been determined, the bleed-off rate required to maintain the solids accumulation below this maximum level can be calculated mathematical formula for the bleed-off rate with respect to the evaporation rate of an open cooling water system is:

$$B = \underline{E}$$

$$C - 1$$

where: B = bleed-off rate, gal/mm (L/min)

E = evaporation rate, gal/mm (L/min)

C = cycles of concentration

The purpose of bleed-off is to remove dissolved solids in order to maintain a maximum level, determined by the maximum recommended cycles of concentration. To maintain this constant maximum level of solids, the amount of solids entering the system must be equal to the amount of solids leaving the system. This can be expressed mathematically as:

Where: C = cycles of concentration

B = bleed-off rate, gal/mm (L/min)M = makeup water, gal/mm (L/min)

X =solids concentration of makeup water, (ppm, mg/L or g/gal)

The makeup rate to an open cooling water system is proportional to the load on the system and is equivalent to the evaporation rate plus any losses of drift, overflow or bleed-off. This is expressed as:

$$M=E+B$$
 (equation 8.2)

Where: M = total makeup rate and E = evaporation rate.

Substituting in equation 8.1, we obtain:

$$BCX = (E + B)X$$

Solving for *B* gives:

$$B = \underline{E}$$

$$C - 1$$

The bleed-off is a total of all water losses from the recirculating systems such as leaks at pumps, overflow, windage drift, and actual bleed. All these together should be sufficient to keep the cycles of concentration below the recommended maximum.

To determine if the total bleed-off from a system is adequate, the cycles of concentration are measured by a simple chloride test. Therefore, a measure of the chlorides in the recirculating water will tell very accurately how much the makeup water has concentrated in that system.



The cycles of concentration are found by comparing the chlorides of the makeup water with the chlorides of the recirculating water:

Cycles of concentration = <u>chlorides in recirculating water</u> chlorides in makeup water

Scale Control. Bleed-off is necessary to prevent deposits of mineral salts as a scale. Scale inhibitors must be used, however, to minimize bleed-off water losses and to permit operation at as high a solids concentration as possible, as outlined in table 8.2. Without scale inhibitors, it would not be possible to accumulate bicarbonate alkalinity and hardness beyond limits that are much lower than those outlined in table 8.2.

Acid Feed. One method of inhibiting scale is by using acid to control the Langelier saturation index. Acids neutralize the bicarbonate alkalinity. Acids can be used to maintain the pH value as close to 7.0 as possible with the alkalinity below the saturation level. This method, however, requires very careful pH and alkalinity control and, most important, careful and controlled feed of acid to avoid excessive corrosive conditions.

Water Softeners. Another way to control scale in open recirculating water systems is by using ion-exchange water softeners. By reducing the hardness, higher cycles of concentration can be established without exceeding the pH of saturation. However, to be effective, this method must include simultaneous feed of acid to reduce the alkalinity. Therefore, it offers no further advantage over alkalinity reduction without softening. Ion-exchange softeners operate at less than 100 percent efficiency throughout the softening cycle. Therefore, trace quantities of hardness bypass the softeners before regeneration.

8.2 Chemical Inhibitor Treatment of Open Recirculating Water Systems

Scale Inhibitors, Dispersants and Deposit Control Agents. The most economical and effective method to control scale is to use scale inhibitors with or without alkalinity reduction. Scale inhibitors, when added to the recirculating water at very low levels, 1 to 20 mg/L, will reduce the scaling tendency. This is accomplished by holding the scale-forming minerals in solution beyond their saturation level, forming supersaturated solutions, by interfering with the growth of scale crystals and formation of scale, or by dispersing the particles of scale and preventing them from adhering to heat-transfer surfaces. In practice, scale inhibitors most likely act in all three ways, thereby preventing scale formation of carbonate, silicate, and sulfate salts of calcium and magnesium. Modern inhibitors also act to control general and specific deposits and risks of fouling, including bio-fouling.

The first scale inhibitor used was sodium hexametaphosphate, which when added to water at only 2 to 3 mg/L, was found to inhibit precipitation of calcium carbonate from supersaturated solutions. This phenomenon was called "threshold treatment" since the polyphosphate holds calcium carbonate in solution at the "threshold" of precipitation. This was later applied to cooling water treatment when polyphosphate became widely used as an inhibitor for scale as well as corrosion. Polyphosphates are still used today, in the range of 0.5 to 5 mg/L, to effectively inhibit scale in condenser water systems. There are, however, some disadvantages to polyphosphate scale inhibitors. These products tend to hydrolyze and revert to the orthophosphate form, which is ineffective as a threshold scale inhibitor. In fact, precipitates of calcium and magnesium orthophosphates can form, causing soft scales on heat-transfer surfaces called "sludge."



In addition, overfeed of polyphosphates in excess of 20 mg/L can result in the formation of insoluble calcium polyphosphate sludge. Finally, the ability of polyphosphates to hold calcium carbonate in solution diminishes significantly with high pH conditions (above 8.0) in recirculating cooling water systems.

Since the 1960s other (superior) scale inhibitors have been developed and new materials regularly enter the market. *Polyacrylate* (and their co- and ter-polymer derivatives), *phosphonate*, *polymaleic acid* and *phosphinocarboxylic acid* chemistry have proved to be significantly more effective than polyphosphates without the above disadvantages. Often, synthetic polymers, such as low-molecular-weight polyacrylates, polymethacrylates, polymaleates, polyhydroxy alkyl acrylates, and polyacrylamides are formulated with polyphosphate and other inorganics to provide multi-purpose inhibitors.

Some of the most widely used organic substances for both scale and corrosion control are the various organic phosphonates. In particular, ATMP, HEDP and PBTC phosphonates are used at very low levels (3 to 5 mg/L as "active" products), as threshold treatments and crystal modifiers to prevent precipitation of calcium carbonate, sulfate and phosphate.

All these polymers, phosphonates and organic phosphates have the distinct advantage of excellent scale-inhibiting properties over a wide range of pH and temperature conditions without the disadvantages of inorganic polyphosphates mentioned above. Many of the polymers, copolymers, and ter-polymers used today are very effective zinc, iron and phosphate sludge inhibitors, stabilizers, or deposit control agents, as well as basic calcium carbonate scale inhibitors.

Corrosion Inhibitors. Just as in boilers corrosion in open cooling water systems is controlled with both environmental stabilizers and corrosion inhibitors. In open cooling water systems, however, oxygen cannot be economically removed with oxygen scavengers because these systems are constantly aerated. Therefore, corrosion inhibitors that are effective in oxygen-containing environments must be utilized.

Also unlike boilers, recirculating cooling water systems contain various types of metals and alloys, and inhibitors and environmental conditions maintained must be compatible with these multimetallic systems. A particular problem associated with these systems is galvanic corrosion caused by bimetallic couples.

Treatment of recirculating cooling water must first include control of the pH value for both scale and corrosion control. A pH value within the range of 6.5 to 9.0 is usually maintained depending on the type of corrosion and scale inhibitor used. Lower pH values tend to render the recirculating water excessively corrosive, while higher pH values will result in both amphoteric metal corrosion (as with zinc, brass, and aluminum) and scale-forming conditions.

In areas where the atmospheric environment is such that acid conditions develop in open cooling water systems, neutralizing substances, such as caustic soda and sodium carbonate (soda ash), can be used to maintain the desired pH value in the neutral range. These conditions can be found in large urban areas or at locations subject to acid fumes from an adjacent boiler stack or incinerator. Conversely, in areas where the makeup water is excessively alkaline, it may be necessary to add acid to maintain the desired pH range for control of scale, as previously outlined.

Within the pH range of 6.5 to 9.0, corrosion is controlled by corrosion inhibitors added to the recirculating water. Inhibitors are substances that do not necessarily alter the environment, but do act as a barrier between the corrosive medium and the metal surface. These materials, when added to the recirculating water, form a protective barrier on the metal surface either by chemical reaction with the metal surface or by physical or chemical adsorption on the metal surface. An actively corroding metal can be rendered passive though the use of inhibitors that react in this manner.



There are many types and combinations of corrosion inhibitors used for open cooling water systems. Basically they fall under four categories, *inolybdate*, *zinc*, *phosphate* and *organic inhibitors*.

Molybdate Inhibitors. Molybdate inhibitors depend upon sodium molybdate as a weak oxidizer for ferrous metals promoting a complex passive oxide film. Molybdates are used in combination with other inhibitors such as zinc, phosphate, phosphonates and organics for synergistic effect to produce highly effective corrosion inhibitor formulations. These formulations of inhibitors have a total effect that is greater than the sum total effectiveness of each individual component and are called synergistic blends. These blends also will include nonferrous metal inbibitors such as *mercaptobenzothiazole*, *benzotriazole* and *tolyltriazole*. These are necessary to protect copper and copper alloys such as yellow brass, bed brass, and admiralty metal.

The molybdate inhibitor blends are usually used at low levels in open cooling water systems, typically maintaining 5 to 10 mg/L as sodium molybdate. However, there are many programs employing organic polymers (All-Organic's) that contain extremely low levels of molybdenum. Here, the typical level in the cooling system is, perhaps, only 1.0–1.5 ppm as Mo. The molybdenum is acting primarily as a "tracer", as it is capable of being easily and accurately tested. There is a secondary benefit, in that the Mo acts as a synergiser to enable other (organic) inhibitors, such as *totyltriazole* (TTA) for copper and *hydroxyphosphinocarboxylic acid* (HPCA), for iron/steel, to function better.

Zinc Inhibitors. Some of the most effective inhibitors use zinc as a cathodic inhibitor in combination with other inhibitors which synergize the overall effectiveness of the inhibitor blend. Some blends are *zinc-silicate*; *zinc-phosphonate*; *zinc-molybdate*; *zinc-polyphosphate-organic* and various *zinc-organic-phosphate* combinations.

The concentration of zinc is usually held to a maximum of 2-5 mg/L, depending upon the type of formulation. The United States Public Health Service Drinking Water Standards limit the zinc of drinking water to 5.0 mg/L, and where this criterion is observed, the zinc should be held to this maximum level. In some cases, zinc discharged even at this level can be toxic to aquatic life. Therefore, discharge to fishponds, streams, and other public waters should not include even this amount of zinc.

Some discharge criteria limit the permissible zinc concentrations to 1.0 mg/L zinc, or less. In this case, non-zinc inhibitors should be used.

Phosphate Inhibitors. Phosphate inhibitor blends are used in alkaline corrosion inhibitors systems combined with polymers that inhibit formation of phosphate sludge. With the development of very effective phosphate scale inhibitors and dispersants such as the copolymers of acrylic acid and sulfonic acid polymer and sulfonated polystyrene and maleic acid phosphate based inhibitors have gained wide acceptance. The ortho-phosphate levels maintained vary from 5 to 20 mg/L. These inhibitors are most effective at high pH and alkalinity and are usually used at pH 8.0-9.0. The formulations require increased scale control from improved polymer and phosphate blends. The organic azole nonferrous metal inhibitors are also necessary for complete protection.

Organic Inhibitors. These are basically fully organic inhibitors that are biodegradable and relatively nonpolluting. Of course, they will add some foreign organic substances to cooling water discharge, but the relative tolerance is better than molybdate, phosphate or zinc compounds.



The organic inhibitors include combinations of various organic and inorganic compounds that have been known to be effective corrosion inhibitors and that tend to be synergistic when used in combinations. Materials include the *azoles* and *hydroxyphosphinocarboxylic acid*.

Corrosion Testing. The relative performance of the types of programs available is based on actual field experience and corrosion monitoring. This can be determined by inserting corrosion test coupons in the open recirculating cooling water system. This corrosion test method has been described by the National Association of Corrosion Engineers (NACE) and is consistent with the ASTM standard "Corrosivity Testing of Industrial Cooling Water (Coupon Test Method)."

The test coupon is placed in the recirculating water system in a test coupon "rack". The corrosion test report will include the calculated corrosion rate in mils per year or micrometers per year and other pertinent data such as depth of pits, variations, and types of corrosion deposits.

The corrosion rate of mild steel for a 30-day exposure time in an open recirculating cooling water system is generally rated to be acceptable below 2.0-4.0 mils per year (mpy) and excellent if below 1.0-2.0 mpy.

The corrosion rates for copper would be, perhaps, 10% of those for mild steel.

8.3. Control of Organic Growths. In Open Recirculating Water Systems

Open recirculating water systems are continually exposed to the ambient air and its contaminants. Among those contaminants are microbiological organisms, which under favorable conditions, will grow and flourish in the warm cooling tower water. The major forms of biological organisms that thrive in cooling tower waters are the bacterial slimes, algae, and fungi. The spores and seeds of these organisms are present in the atmosphere attached to particles of dust, dirt, pollen, and other airborne particulates. When washed out of the air at the cooling tower they find a favorable environment to grow and multiply. These growths cause serious problems of corrosion, fouling, blockage, and accelerate buildup of deposits. Such growths not only interfere with water flow but also reduce heat transfer and increase energy losses.

Biological growths can be controlled by substances capable of limiting their growth or outright killing the organisms without harming the system or the environment. These substances are called "microbjcjdes" "biocides," "slimicides," "algicides," and "fungicides." They fall into the general classification called "pesticides" which are controlled and registered by the Environmental Protection Agency. Pesticides used in cooling water treatment are more commonly referred to as "microbicides".

A disinfecting dosage is one from which a complete kill can be expected within a few hours, provided the sterilizing solution comes into contact with the organism. An inhibiting dosage is the level at which the growth of the organism can be prevented or minimized once the dosage is removed from the system. A biostatic dosage is one that is applied (usually continuously) to maintain microorganisms as tolerably low levels. In general, only oxidizing biocides are applied as biostats, due to their low feed rate and, generally lower cost compared to non-oxidizers.

Oxidizing biocides. The most widely used microbiocide for recirculating water systems is chlorine, an oxidizing biocide. Chlorine used in excess will damage wood and organic fill in cooling towers. Usually it is only used in systems large enough to justify equipment for its controlled feed. Where chlorine is used on a continuous basis, the concentration of free chlorine should be maintained at 0.3 to 0.5 mg/L to minimize the attack on materials of construction. For cleaning purposes, shock feed of up to 50 mg/L can be used, provided this high chlorine content is held for no more than 8 h and the system is thoroughly flushed and drained, to remove dead organic matter and excess chlorine.



The use of chlorine on an intermittent basis has been found to be effective in inhibiting the growth of a particular biological organism while at the same time minimizing the disadvantages of continuous chlorine feed. Chlorine is a very strong oxidizing agent, and so it is excessively corrosive to metals and damaging to cooling tower lumber and organic fill. Furthermore, it is very difficult to control the feed of chlorine at levels, which will be effective in limiting organic growth while not attacking the materials of construction.

Bromine, less corrosive than chlorine, is more commonly used and is more effective than chlorine at the operating pH range of cooling towers today.

The microbicides most extensively used in cooling towers, air washers, and other open recirculating water systems for HVAC are *bromine*, *quaternary ammonium compounds*, *organo sulfur compounds* and *aldehydes*.

The most effective combinations include *hydroxyphosphono acetate* with the organic polymers and triazoles.

Other effective microbicides are *organo-tin copper* compounds used with the *quaternary ammonium compounds*, also *dibromo~3~nitriloproprionamide*, mixed *isothiazolins* and *l-bromo-3-chlorodimethylhydantoin*.

Nonoxidizing microbicides are best applied to clean systems to inhibit, i.e., prevent, an organic growth rather than to kill or remove an existing growth. Sterilizing dosages of these biocides can be used to kill an organism, but usually penetrating agents are needed to assist the biocides in penetrating the mat of the organism, especially when the growth is of the algae type, which forms layers of thick mats on the surface of the equipment.

Cleaning and disinfecting a contaminated cooling water system requires a significant amount of physical flushing and removal of organic matter to prevent re-infestation. Care must be taken to circulate the solution through the many nooks and crannies in these systems where growths can adhere and eventually grow to re-infest a system. Correct selection and application of microbicides is a critical issue and some level of knowledge and practical experience is required. Selection guidelines are just that, a starting point, and to ensure an effective sterilizing dosage and inhibiting dosage for most of the organisms found in HVAC open recirculating water systems requires the expertise of a water treatment professional.

The manner of feeding biocides to a system is also very important. Often the continuous feed at low inhibiting dosages is not particularly effective and can be very costly. Organisms tend to build up immunity to a single biocide, and low dosages may even encourage the growth of some organisms. Therefore, a shock dosage at a level high enough for a bacterial kill is more effective than a continuous dosage at a low level. In addition, occasional change of the type of biocide used will prevent development of microbial immunity.

Treatment of HVAC systems should include periodic shock dosages of a biocide only when experience indicates a need.

Bacteria Test. Test methods are available for monitoring the recirculating water to obtain a total bacteria count and predetermine the need for biocides. Field methods include test strips, dipsticks, IME glass vials and ATP meters. Laboratory methods include plate counts.

Tests made periodically during operation of the system will provide a history that will indicate if there is an increase in the bacteria count during any particular season, showing the possible need of a biocide.

These tests are also used to determine the effectiveness of a biocide program over time and indicate when treatment programs should be changed or improved.



The biocide program performance should be evaluated as follows:

Total Bacteria Count	Condition
0 -10 ² colonies/mL 10 ² -10 ³ colonies/mL 10 ⁴ -10 ⁵ colonies/mL 10 ⁵ -10 ⁶ colonies/mL Above 10 ⁶ colonies/mL	Excellent control Warning, but No Serious Fouling Maximum. 10 ⁴ for Healthcare, 10 ⁵ for Commerce/Industry Fouling Anticipated and possible Health Risk Serious Risk of Fouling and Pathogens

8.4 Infection Control in Open Recirculating Water Systems

The control of infection from water systems requires environmental maintenance and surveillance. Awareness of the part played in the spread of infectious diseases by pathogenic organisms, by dirty and poorly designed or maintained cooling systems and other HVAC systems, has grown significantly over recent years. Publicity, litigation and general environmental and health concerns have added to the awareness. Consequently, in the U.S. many rules and codes now exist requiring owners and operators to improve operations by retro-design changes and to regularly clean and disinfect their cooling systems. Also required is the application of a comprehensive water treatment program and record keeping in a suitable logbook.

Such rules are, as yet, not as stringent as those in some parts of Western Europe and Australia and New Zealand, but are likely to do so, in the not-so-distant future. As a result, regular cleaning and disinfection using the Wisconsin Protocol, or similar, is desirable.

Protocols for cleaning and disinfection programs. These may vary depending upon whether the disinfection procedure is part of a scheduled maintenance program, or an emergency decontamination response. Commonly however the disinfection procedures fall into three parts.

- 1. **Pre-chlorination stage** is designed to provide disinfected water, either remotely stored, or obtained by the chlorination of the water in the cooling tower, prior to cleaning work being carried out. Typically water is considered disinfected if a 20 ppm free reserve of chlorine is maintained for at least one hour. Lower levels of free reserve may require a much longer period for initial disinfection.
- **2. Draining & cleaning stage**. Here, the disinfected water is circulated for 1-4 hours, then drained and the system physically cleaned. Bio-dispersants may be employed.
- 3. Disinfection, recommissioning and water treatment reinstatement stage. The system is refilled and disinfected for the required period, then put back into service. Standards again vary. Typically for routine maintenance the water is considered disinfected if a 5 ppm free reserve of chlorine is maintained for at least one hour. If the system is being decontaminated because of positive Legionella results, then the requirement is often 10 ppm free reserve for at least 1 hour.

Note that during any cleaning and disinfection procedure, the application of disinfectant and dispersant may dislodge sufficient amounts of solids to clog screens and filters. All screen and filters should be inspected periodically during the emergency procedure, and during general use they should be cleaned as needed. Also, to assure adequate chlorine contact throughout the tower, be sure that spray nozzles and other mechanical components are operating properly. During the water treatment reinstatement stage, implement the chemical treatment program in accordance with instructions from your Water Treatment Contractor.



The deposit & corrosion inhibitor products used should not interfere with the action of the biocidal compounds in regards to their effectiveness against Legionella.

Legionella Testing. Monitoring the total bacterial count in the cooling system water is a useful indicator of the general effectiveness of the biocide treatment program and to the possible need for modification, however there is no definitive correlation between total plate count and the presence of Legionella.

With regard to Legionella testing, a positive result of below $1x \cdot 10^2$ in cooling waters tends to reflect only that the system is a potential amplifier for higher numbers and some inspection and future re-testing may be necessary. Where the positive result is above $1x \cdot 10^2$, this usually indicates a cleaning and disinfection program is necessary. This is especially true if the positive result is for *Legionella pneumophila sero-group 1*. Actions based on absolute numbers are not necessarily useful, rather, if during a sampling and testing program, more than 30% of samples are proved positive, this is cause for concern.

Legionella species do not respond readily to most traditional biochemical tests used for identification of bacteria. Confirmation of isolates is achieved by serological methods, or the use of more sophisticated tests. There are several tests currently employed, each with their own benefits and limitations, including:

- Standard culture method
- Legionella rapid assay method.
- Direct fluorescent antibody (DFA) method.

Many authorities still do not advocate regular testing and although unplanned and once-off tests are of minimal value, however, it should be remembered that Legionella organisms could kill you. Consequently, it is recommended that all new cooling systems and cooling systems that have shut down for an extended period of time be tested for the presence of Legionella. It is also recommended that all cooling systems be assessed to determine risks associated with Legionella. Those cooling systems found to be at high to moderate risk should be tested a minimum of 4 times a year. All other cooling systems should have a test performed twice a year, as part of a planned program. This testing will allow for up-to-date record keeping and any trend to be identified. Also, it will help confirm the quality, or otherwise, of the overall infection control program.

Testing for Legionella requires special sampling techniques and usually requires a period of 14 working days from receipt of the sample to obtain a result. A positive result will include an identification of the Legionella species, and typically also of the sero-groups 1-6, plus a determination of the number of the bacterium per 1 milliliter of the original sample.

8.5 Control of Muds and Other Treatments

Mud and Dirt Control. Deposits of mud, dirt, and foreign suspended matter washed out of the atmosphere into open recirculating Water systems can be as troublesome as scale and must be controlled for efficient operation of heat-transfer equipment. In the past, treatment for mud, dirt, and silt consisted only of physical removal with filters and separators or manual cleaning.

Now soluble polymers used in water clarification are applied to cooling waters with significant success. These polymers are high-molecular-Weight polyelectrolytes that attract small dirt particles, forming a larger mass. This process is called "coagulation." The larger mass, called an "agglomerate," has a tendency to "float" or remain non-adherent to piping surfaces, and it does not compact into a mud.



Coagulant-type polyelectrolytes can be used for mud and dirt control at dosages as low as 0.5 to I mg/L. Coagulants usually are best applied in a shock manner on a periodic basis rather than continuously, while dispersants are applied on a continuous basis for maximum results. Coagulants may be included in the proprietary corrosion and deposit inhibitor formulation.

Disperants are a very different type of mud and dirt control agent. They have the opposite effect to a coagulant and prevent formation of mud deposits because of their ability to "repel" particles. Dispersants prevent the formation of larger agglomerates and thus their compacting into a mud. This causes the particles to be held in suspension, so they are more readily removed with normal bleed-off.

Cooling Tower—Evaporative Condenser Treatment. A complete treatment program for condenser water systems for HVAC equipment should include all the materials required to prevent corrosion and deposits. In addition, parameters should be given for bleed-off control to avoid excessive accumulation of minerals in the cooling tower and evaporative condenser circuit.

Air Washer and Surface Spray Treatment. Treatment of air washers and surface spray units will be similar to that of open cooling tower and evaporative condenser systems. The essential difference is that the former systems are subject to a wide variation of conditions with respect to temperature and humidity.

8.6 Feed and Control of Cooling Water Treatment Programs

Test Controls. Simple, easy-to-use test kits are available for regular testing of inhibitor levels and chlorides for cycles of concentration to control bleed-off. The tests should be made daily to ensure adequate control. Additional tests are made by the water service company to verify the accuracy of field test results.

Feed Methods. Treatments may be fed into systems simply by shock feed through any convenient opening, usually in the tower or condenser pan. This requires frequent additions at high levels to ensure maintenance of minimum levels of inhibitor in the recirculating water. For example, to maintain a minimum of 300 mg/L of a corrosion inhibitor in a cooling tower will require shock dosages at levels up to 664 mg/L every day. This method can be very costly and wasteful, as a significant over-treatment is required to maintain the minimum level of 300 mg/L. To conserve treatment, therefore, proportional feed methods should be used.

Shock methods of feed are required, however, for certain types of treatment such as cleaners and biocides. These are fed at high levels on an intermittent basis to effect a cleanup action or biological kill, rather than to continuously maintain minimum levels.

- 1. Canister-type feeders: To obtain a more continuous or gradual feed, the canister-type feeder is used. This feeder comes in various designs. All consist of a can, or reservoir, containing treatment that is gradually dissolved or diluted so that it is fed slowly over a long time.
- 2. Proportioning feed methods: A more accurate method of feeding treatment is by means of a proportioning chemical feed pump. Proportioning feed pumps add treatment directly in proportion to the loss of treatment from the system, thereby maintaining a precise and consistent minimum treatment level. This avoids the excessive losses of shock feed or less accurate canister feeders. A simple proportioning feed method utilizes a chemical feed pump interlocked with the recirculating water pump on the cooling tower, evaporative condenser, or spray cooler.



The pump adds treatment directly from the drum or mixing tank. This system automatically injects the necessary treatment into the recirculating condenser water line, based on an assumed continuous-load factor, Sufficient water is bled from the system on a continuous basis when the condenser water pump is on. This maintains the cycles of concentration at a safe operating level. Treatment is then fed continuously in proportion to the bleed rate so as to make up for loss of treatment in the bleed-off

One of the most basic, fundamental, and universally adaptable fully automatic systems uses the water flow meter as a control. Since the rate of makeup water is proportional to evaporation and the actual load on a condenser water system, this is a fully automatic control system, independent of the quality of makeup water that requires no additional instrumentation for accuracy other than pH control, if needed. With this system, sufficient water can be bled automatically from the recirculating water to maintain the maximum cycles of concentration permitted. Treatment is then fed in direct proportion to bleed to replace any that is lost in the bleed-off.

Another widely used automatic proportioning feed-and-bleed system uses a total dissolved solids (TDS) analytical instrument as a control. This is commonly called the "conductivity controller" or "TDS controller." Since the dissolved mineral solids in water are directly proportional to the electrical conductivity, the conductivity measurement can be used to determine any variation in dissolved solids. Because the dissolved solids content increases in proportion to the evaporation and load on the cooling system, this system is fully automatic. In this system, bleed-off is activated when the TDS controller detects high TDS content so that the maximum permissible cycles of concentration are maintained. Treatment is then fed in direct proportion to bleed, to replace any that is lost in the bleed-off.

Another controller used for HVAC systems, the pH controller is needed where pH control is required because of atmospheric conditions and/or the quality of makeup water or the type of program used. The controller automatically maintains the pH value of the recirculating water at the desired level and, when necessary, activates a chemical feed pump to add acid or alkali.

Controllers are capable of being interconnected with building management systems (BMS) for rapid real-time remote monitoring and control through the computer. Chemical treatment can be controlled by constant monitoring of treatment levels in the cooling tower directly using auto analyzers, which then control chemical feed. Other systems are available which control chemical feed based on actual corrosion rate. The corrosion rate monitor is set to control and add treatment as needed to maintain a specific corrosion rate setting.

Biocides are added using timer controls, which add biocides at specific times and days of the week as needed. All of this can be monitored and controlled through the computer.

8.7 Treatment of Closed Recirculating Water Systems

General. The need for treatment in closed recirculating water systems has frequently been questioned. It is often observed that because such systems are closed, they do not take on the impurities, excess minerals, and dissolved corrosive gases, which are the prime causes of scale and corrosion.

Operating experience, however, indicates that much more makeup is used in closed systems than one would anticipate. For example, a very slow drip past packing glands of recirculating pumps to maintain lubrication at the rate of 1 oz/min (30 mL/min) will require a makeup rate of 337.5 gal/month (1260 L/month), or 4050 gal/year (15,000 L/year).

Experience has sometimes shown that the makeup rate to closed systems can average 100 percent of the volume per month. The makeup water is required because of water losses at packing glands and draining for maintenance and repairs of pumps, valves, or controls.



With makeup water, dissolved minerals and oxygen are introduced. The calcium and magnesium hardness will deposit at heat-transfer surfaces and will accumulate as more makeup is introduced. All closed systems must "breathe," and expansion tanks are a source of atmospheric air and corrosive gases.

Galvanic couples of copper, iron, brass, and aluminum are commonly used in closed systems without dielectric fittings, which result in a higher rate of corrosion of the less noble metal at the couple. Therefore, it is generally accepted that treatment of these systems is required to prevent problems of corrosion and deposits as well as to maintain clean, efficient heat-transfer surfaces."

Before closed recirculating water systems are treated to prevent scale and corrosion, it is essential to clean them thoroughly. All types of debris may enter a system during construction, and these must be removed. In addition, protective oil- based coatings and mill scale must be removed from the interior of the piping to avoid corrosion and damage from these sources. Black magnetic iron mill scale is a particular problem in closed systems and must be removed not only to prevent corrosion and heat-insulating deposits but also to avoid damage to pumps, packing, and mechanical seals.

Materials most effectively used for such cleanouts are low-foaming detergents built with strong dispersants to prevent resettling. Dispersants are an important part of the closed system cleaner because they help to remove fine, black magnetic iron oxide particles by suspending them throughout the body of the recirculating cleaning solution and preventing them from settling and plugging. The detergent-dispersant cleaner should be added to the recirculating water at the dosage recommended by the manufacturer for 3 to 4 h. Then drain, refill, and recirculate as fast as possible, all at the same time, to obtain maximum flow through all portions of the system and to avoid pockets and dead-end locations where sediment can be trapped. The system should be flushed out until all traces of residual detergent and suspended matter are gone.

After cleanout, closed systems must be treated for control of corrosion and deposits. First, the makeup water should be analyzed to determine if pretreatment, such as a water softener, is required. Then treatment must be added to prevent further corrosion and deposits.

Closed systems are filled with fresh water and corrosion and deposit inhibitors or, under freezing conditions, with a solution of water and an inhibited glycol antifreeze compound. Antifreeze solutions are being used with increasing frequency to protect exposed piping of closed hydronic hot-water or chilled-water systems from freezing and rupturing.

Where antifreeze solutions are required, an inhibited ethylene glycol or propylene glycol could be used at a minimum concentration of 30 percent. Specific HVAC-grade glycol antifreeze should be used, not automotive- grade. Samples of solutions should be analyzed on a periodic basis to ensure that the inhibitor has not been depleted or decomposed.

Closed systems filled with raw water must be treated further for corrosion and deposit control.

High~Temperature Hot-Water Heating Systems- High-temperatures hot-water (HTHW) heating systems are defined as those operating above 350°F (178°C) and 450 lb/in² (3.00 kPa). These systems are frequently used to provide central heating for large complexes or campus-like situations. Unless zeolite-softened water is used in these systems, the high temperature encountered, combined with the large volume of water in the system, will cause scale deposits to accumulate at the heat-transfer surfaces of the HTHW boiler. The ratio of water volume to heat-transfer surface area is such that even the initial scale deposits would be sufficient to cause significant interference with heat transfer.

Additional treatment should include an oxygen scavenger such as diethylhydroxylamine or sodium sulfite. The latter is preferable in systems containing nonferrous metals. Caustic soda should be used to maintain the pH value of the water at 8.0 to 10.0.



Dispersants and scale inhibitors are used to maintain clean heat-transfer surfaces. These consist of thermally stable inhibitors such as polyacrylates, polymethacrylates, and phosphonates.

Medium~Temperature Hot-Water Systems. Medium-temperature hot-water (MTHW) heating systems are defined as those operating at 250°F (120°C) up to 350°F (177°C) with pressures above 30 lb/in² (206 kPa). This kind of system is treated in the same way as HTHW systems. Oxygen scavengers, such as sodium sulfite or diethylhythoxyl amine, control corrosion and pitting, and the pH value is maintained at 8.0 to 10.0 with caustic soda or a similar alkali. The system should be filled with zeolite-softened water to avoid scale deposits on heat-transfer surfaces. Scale inhibitor and dispersant should be added in the form of thermally stable inhibitors, as described above.

Low-Temperature Hot-Water Systems. Low-temperature hot-water (LTHW) systems are defined as those operating below 250°F (120°C) with maximum water pressure of 30 lb/in² (206 kPa). In low-temperature systems, bimetallic couples of steel, copper, brass, and aluminum are frequently used. The recirculating water in an LTHW system is best treated with corrosion inhibitors such as a sodium nitrite-borax combination. This inhibitor and similar inhibitors are not used at temperatures above 250°F (120°C) because of their questionable stability at higher temperatures. Apparently the film-forming mechanism is severely restricted at higher temperatures so that there is spotty pitting and even decomposition of the inhibitor in the case of nitrite inhibitors.

Sodium nitrite-borax inhibitor systems and other nitrite-based compositions are used at 3000 to 4000 mg/L at temperatures above 180°F, while 1000 to 2000 mg/L is sufficient for systems operating below 180°F. With nitrite-based treatments, it is important to use specific copper and brass inhibitors such as mercaptobenzothiazole or phenyltriazoles to minimize copper attack and copper-induced pitting of steel.

Other corrosion inhibitors that are available in proprietary blends include phosphate organics, amides, silicates, benzoates, phosphonates, and molybdates, as well as various combinations of these with other organics. The concentrations recommended by the suppliers of these inhibitors should be followed to obtain good corrosion control.

Inhibitors for control of scale and deposit are used along with the corrosion inhibitors and are usually included in the proprietary blend. Scale inhibitors for LTHW heating systems include sodium polyacrylates, polymethacrylates, polymaleates, sulfonated polystyrene, carboxymethylcellulose, lignins, and phosphonates. Some of these materials also act as dispersants which prevent sedimentation of fine particulate matter and provide excellent scale and deposit control When these inhibitors are used, it is typically not necessary to soften the makeup water required to compensate for "normal" losses such as drips, leaks, repairs, etc.

Chilled-Water Systems. Chilled-water systems operate below 140°F (60°C), usually in the range of 44 to 54°F (10 to 12°C) for comfort cooling. Sodium nitrite-borax inhibitors and other nitrite-based blends are used in the range of 500 to 1000 ppm with the pH maintained within the range of 7.0 to 10.0. It is important that nitrite-based inhibitors include nonferrous-metal inhibitors to reduce nitrite attack on solder and other nonferrous metals. Among these inhibitors are borax, sodium benzoate, phosphates, and copper inhibitors, mercaptobenzothiazole, or phenyltriazoles. Chilled-water systems invariably contain components of multi-metallic construction, which include iron, steel, copper, brass and aluminum, and which require balanced formulated inhibitors to ensure that all metals are individually protected, as well protecting against the galvanic couples of these metals. Other inhibitors for chilled-water systems are organics blended with phosphates, silicates, or molybdate, sodium benzoate, organic phosphonates, and organic amines such as methyl glycine and imidazoline.



The corrosion inhibitor or inhibitor blend may be combined with dispersants and deposit inhibitors for a complete treatment. The dispersants are the same as those used in hot-water systems.

Closed-Circuit Coolers. Closed circuit coolers are closed condenser water systems, which are combined with an evaporative cooler. The closed condenser water circuit is treated the same as the closed chilled-water circuit with formulated inhibitors for control of corrosion and deposits.

Solar Heat-Exchange Systems. Another type of closed system being used with growing frequency is the energy-saving solar heat-exchange circuit. These systems also require treatment for control of corrosion and deposits. The most effective treatments are those used for chilled-and hot-water heating circuits.

Test Controls. Quality tests on samples of closed system treated water should be made at a minimum of monthly intervals to record conditions and be assured correct treatment levels are being maintained. At a minimum tests should be made for inhibitor level and p11. The testing services offered by the water treatment supplier should be monthly, as a minimum, and include a complete water analysis, including inhibitor levels.

Method of Feed. Treatments are applied to closed systems by several convenient means. They may be added directly through any opening into the system, such as at the expansion tank or open reservoir.

For very small but "tight" systems, the use of a simple stirrup pump or force may be employed to inject treatment directly through a drain valve or hose cock.

In most instances, however, it is more convenient to install a bypass feeder across the recirculating pump. With a differential in pressure between the discharge side and the suction side of the recirculating pump, the water in the system is forced through the bypass feeder, so the treatment is injected directly into the system. The maintenance of a treatment program for closed systems is relatively simple, and the benefits obtained in corrosion protection and efficient operations are substantial.

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