

## WATER, INDUSTRIAL WATER TREATMENT

Abundant supplies of fresh water are essential to the development of industry. Enormous quantities are required for the cooling of products and equipment, for process needs, for boiler feed, and for sanitary and potable water supply.

### 1. Water Impurities

Water impurities include dissolved and suspended solids. Calcium bicarbonate is a soluble salt. A solution of calcium bicarbonate is clear, because the calcium and bicarbonate are present as atomic-size ions that are not large enough to reflect light. Suspended solids are substances that are not completely soluble in water and are present as particles. These particles usually impart a visible turbidity to the water.

### 2. Clarification

Suspended matter in raw water supplies is removed by various methods to provide a water suitable for domestic purposes and most industrial requirements. The suspended matter can consist of large solids, settleable by gravity alone without any external aids, and nonsettleable material, often colloidal in nature. Removal is generally accomplished by coagulation, flocculation, and sedimentation. The combination of these three processes is referred to as conventional clarification.

Coagulation involves neutralizing charged particles to destabilize suspended solids. In most clarification processes, a flocculation step then follows. Flocculation starts when neutralized or entrapped particles begin to collide and fuse to form larger particles. This process can occur naturally or can be enhanced by the addition of polymeric flocculant aids.

Table 1 lists a number of common inorganic coagulants. Typical iron and aluminum coagulants are acid salts that lower the pH of the treated water by hydrolysis. Depending on initial raw water alkalinity and pH, an alkali such as lime or caustic must be added to counteract the pH depression of the primary coagulant. Iron and aluminum hydrolysis products play a significant role in the coagulation process, especially in cases in which low turbidity influent waters benefit from the presence of additional collision surface areas.

With aluminum sulfate, optimum coagulation efficiency and minimum floc solubility normally occur at pH 6.0–7.0. Iron coagulants can be used successfully over the much broader pH range of 5.0–11.0. If ferrous compounds are used, oxidation to ferric iron is needed for complete precipitation. This may require either chlorine addition or pH adjustment.

Polyelectrolytes refers to all water-soluble organic polymers used for clarification, whether they function as coagulants or flocculants. Water-soluble polymers may be classified as follows:

*Anionic.* Ionize in water solution to form negatively charged sites along the polymer chain.

## 2 WATER, INDUSTRIAL WATER TREATMENT

**Table 1. Common Inorganic Coagulants**

Name	Typical formula	Typical strength	Typical forms used in water treatment	Density	Typical uses
aluminum sulfate	$\text{Al}_2(\text{SO}_4)_3 \cdot 14 \text{ to } 18\text{H}_2\text{O}$	17% $\text{Al}_2\text{O}_3$	lump, granular, or powder	961–1121 kg/m <sup>3</sup>	primary coagulant
alum		8.25% $\text{Al}_2\text{O}_3$	liquid	1.33 kg/L	
aluminum chloride	$\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$	35% $\text{AlCl}_3$	liquid	1.50 kg/L	primary coagulant
ferric sulfate	$\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$	68% $\text{Fe}_2(\text{SO}_4)_3$	granular	1121–1153 kg/m <sup>3</sup>	primary coagulant
ferric-floc	$\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$	41% $\text{Fe}_2(\text{SO}_4)_3$	solution	1.47 kg/L	primary coagulant
ferric chloride	$\text{FeCl}_3$	60% $\text{FeCl}_3$ , 35–45% $\text{FeCl}_3$	crystal, solution	961–1025 kg/m <sup>3</sup>	primary coagulant
				1.34–1.49 kg/L	
sodium aluminate	$\text{Na}_2\text{Al}_2\text{O}_4$	38–46% $\text{Na}_2\text{Al}_2\text{O}_4$	liquid	1.47–1.55 kg/L	primary coagulant; cold-hot precipitation softening

*Cationic.* Ionize in water solution to form positively charged sites along the polymer chain.

*Nonionic.* Ionize in water solution to form slight negatively charged sites along the polymer chain.

Polymeric primary coagulants are cationic materials with relatively low molecular weights (under 500,000). The cationic charge density (available positively charged sites) is high. Polymeric flocculants or coagulant aids may be anionic, cationic, or nonionic. Their molecular weights may be as high as 50,000,000. Table 2 describes some typical organic polyelectrolytes.

The use of organic polymers offers several advantages over the use of inorganic coagulants:

The amount of sludge produced during clarification can be reduced by 50–90%; the approximate dry weights of solids removed per pound of dry alum and ferric sulfate are approximately 0.11 and 0.23 kg, respectively.

The resulting sludge contains less chemically bound water and can be more easily dewatered.

Polymeric coagulants do not affect pH; therefore, the need for supplemental alkalinity, such as lime, caustic, or soda ash, is reduced or eliminated.

Polymeric coagulants do not add to the total dissolved solids concentration, eg, 1 ppm of alum adds 0.45 ppm of sulfate ion (expressed as  $\text{CaCO}_3$ ); the reduction in sulfate can significantly extend the capacity of anion-exchange systems.

Soluble iron or aluminum carryover in the clarifier effluent may result from inorganic coagulant use; therefore, elimination of the inorganic coagulant can minimize the deposition of these metals in filters, ion-exchange units, and cooling systems.

In certain instances, an excess of primary coagulant (whether inorganic, polymeric, or a combination of both) may be fed to promote large floc size and to increase settling rate. However, in some waters, even high doses of primary coagulant will not produce the desired effluent clarity. A polymeric coagulant aid added after the primary coagulant may, by developing a larger floc at low treatment levels, reduce the amount of primary coagulant required.

Generally, very high molecular weight anionic polyacrylamides are the most effective coagulant aids. Nonionic or cationic types have proven successful in some clarifier systems. Essentially, the polymer bridges the small floc particles and causes them to agglomerate rapidly into larger, more cohesive flocs that settle quickly. The higher molecular weight polymers bridge suspended solids most effectively. Coagulant aids have proven

Table 2. Common Organic Polyelectrolytes

Polymer type	Typical formula	Typical molecular weight	Available forms	Typical uses
	<b>polyacrylamide</b>			
nonionic	$\left[ \begin{array}{c} \text{—CH}_2\text{—CH—} \\   \\ \text{C=O} \\   \\ \text{NH}_2 \end{array} \right]_n$	$1 \times 10^6$ to $2 \times 10^7$	powder, emulsion, solution	flocculant in clarification with inorganic or organic coagulants
	<b>hydrolyzed polyacrylamide</b>			
anionic	$\left[ \begin{array}{c} \text{—CH}_2\text{—CH—} \\   \\ \text{C=O} \\   \\ \text{NH}_2 \end{array} \right]_n \left[ \begin{array}{c} \text{—CH}_2\text{—CH—} \\   \\ \text{C=O} \\   \\ \text{ONa} \end{array} \right]_y$	$1 \times 10^6$ to $2 \times 10^7$	powder, emulsion, solution	flocculant in clarification with inorganic or organic coagulants
	<b>poly(DADMAC) or poly(DMDAAC) polymers</b>			
cationic	$\left[ \begin{array}{c} \text{—CH}_2\text{—CH—CH—CH}_2\text{—} \\   \quad   \\ \text{CH}_2 \quad \text{CH}_2 \\ \diagdown \quad \diagup \\ \text{N} \\ \diagup \quad \diagdown \\ \text{CH}_3 \quad \text{CH}_3 \end{array} \right]_n + \text{Cl}^-$	250 to $500 \times 10^3$	solution	primary coagulant alone or in combination with inorganics in clarification
	<b>quarternized polyamines</b>			
cationic	$\left[ \begin{array}{c} \text{—CH}_2\text{—CH—CH}_2\text{—N—} \\   \quad \quad   \\ \text{OH} \quad \quad \text{CH}_3 \\ \quad \quad \quad   \\ \quad \quad \quad \text{CH}_3 \end{array} \right]_n$	10 to $500 \times 10^4$	solution	primary coagulant alone or in combination with inorganics in clarification
cationic	polyamines $\text{—CH}_2\text{—CH}_2\text{—NH}_2\text{—}$	$10^4$ to $10^6$	solution	primary coagulant alone or in combination with inorganics in clarification

quite successful in precipitation softening and clarification to achieve improved settling rates of precipitates and finished water clarity.

### 3. Precipitation Softening

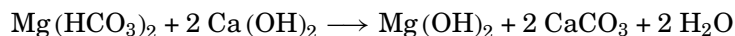
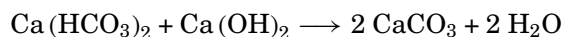
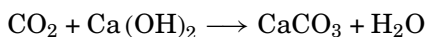
Precipitation softening processes are used to reduce raw water hardness, alkalinity, silica, and other constituents. This helps prepare water for direct use as cooling tower makeup or as a first-stage treatment

## 4 WATER, INDUSTRIAL WATER TREATMENT

followed by ion exchange for boiler makeup or process use. The water is treated with lime or a combination of lime and soda ash (carbonate ion). These chemicals react with the hardness and natural alkalinity in the water to form insoluble compounds. The compounds precipitate and are removed from the water by sedimentation and, usually, filtration. Waters with moderate to high hardness and alkalinity concentrations (150–500 ppm as  $\text{CaCO}_3$ ) are often treated in this fashion.

### 3.1. Cold Lime Softening

Precipitation softening accomplished at ambient temperatures is referred to as cold lime softening. When hydrated lime,  $\text{Ca}(\text{OH})_2$ , is added to the water being treated, the following reactions occur:



Noncarbonate or permanent calcium hardness, if present, is not affected by treatment with lime alone. If noncarbonate magnesium hardness is present in an amount greater than 70 ppm and an excess hydroxyl alkalinity of about 5 ppm is maintained, the magnesium will be reduced to about 70 ppm, but the calcium will increase in proportion to the magnesium reduction.

To improve magnesium reduction, which also improves silica reduction in cold process softening, sodium aluminate may be used. The sodium aluminate provides hydroxyl ion ( $\text{OH}^-$ ) needed for improved magnesium reduction, without increasing calcium hardness in the treated water. In addition, the hydrolysis of sodium aluminate results in the formation of aluminum hydroxide, which aids in floc formation, sludge blanket conditioning, and silica reduction.

### 3.2. Warm Lime Softening

The warm lime softening process operates in the temperature range of 49–60°C. The solubilities of calcium, magnesium, and silica are reduced by increased temperature. Therefore, they are more effectively removed by warm lime softening than by cold lime softening.

### 3.3. Hot Process Softening

Hot process softening is usually carried out under pressure at temperatures of 108–116°C. At the operating temperature, hot process softening reactions go essentially to completion. This treatment method involves the same reactions described above, except that raw water  $\text{CO}_2$  is vented and does not participate in the lime reaction. The use of lime and soda ash permits hardness reduction down to 0.5 g/gal, or about 8 ppm, as calcium carbonate. Magnesium is reduced to 2–5 ppm, because of the lower solubility of magnesium hydroxide at the elevated temperatures.

**Table 3. Typical Softener Effluent Analyses**

Factor	Raw water	Removal of calcium alkalinity cold-lime	Lime–soda softening (cold)	Lime–soda softening (hot) <sup>a</sup>	Lime softening (hot) <sup>a</sup>
total hardness (as CaCO <sub>3</sub> ), ppm	250	145	81	20	120
calcium hardness (as CaCO <sub>3</sub> ), ppm	150	85	35	15	115
magnesium hardness (as CaCO <sub>3</sub> ), ppm	100	60	46	5	5
“P” alkalinity (as CaCO <sub>3</sub> ), ppm	0	27	37	23	18
“M” alkalinity (as CaCO <sub>3</sub> ), ppm	150	44	55	40	28
silica (as SiO <sub>2</sub> ), ppm	20	19	18	1–2	1–2
pH	7.5	10.3	10.6	10.5	10.4

<sup>a</sup>Removal of SiO<sub>2</sub> by the hot process, to the levels shown, may require the feed of supplemental magnesium oxide. Sludge recirculation is necessary. All raw water constituents will be diluted by the steam used for heating by approximately 15% if the process is hot.

### 3.4. Silica Reduction

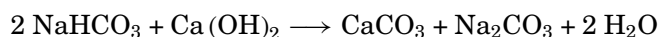
Hot process softening can also provide good silica reduction. The silica reduction is accomplished through adsorption of the silica on the magnesium hydroxide precipitate. If there is insufficient magnesium present in the raw water to reduce silica to the desired level, magnesium compounds (such as magnesium oxide, magnesium sulfate, magnesium carbonate, and dolomitic lime) may be used.

### 3.5. Alkalinity Reduction

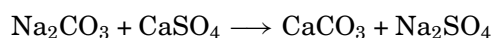
Treatment by lime precipitation reduces alkalinity. However, if the raw water alkalinity exceeds the total hardness, sodium bicarbonate alkalinity is present. In such cases, it is usually necessary to reduce treated water alkalinity in order to reduce condensate system corrosion or permit increased cycles of concentration.

### 3.6. Treated Water Quality

Predicted analyses of a typical raw water treated by various lime and lime–soda softening processes are presented in Table 3. Treatment by lime converts the sodium bicarbonate in the raw water to sodium carbonate as follows:



Calcium sulfate (gypsum) may be added to reduce the carbonate to required levels. The reaction is as follows:



## 4. Filtration

Filtration is used in addition to regular coagulation and sedimentation or precipitation softening for removal of solids from surface water or waste water. This prepares the water for use as potable, boiler, or cooling makeup. Waste water filtration helps users meet more stringent effluent discharge permit requirements.

Filtration does not remove dissolved solids, but may be used together with a softening process, which does reduce the concentration of dissolved solids. For example, anthracite filtration is used to remove residual precipitated hardness salts remaining after precipitation softening.

## 6 WATER, INDUSTRIAL WATER TREATMENT

In most water clarification or softening processes in which coagulation and precipitation occur, at least a portion of the clarified water is filtered. Clarifier effluents of 2–10 NTU may be improved to 0.1–1.0 NTU by conventional sand filtration. Filtration ensures acceptable suspended solids concentrations in the finished water even when upsets occur in the clarification processes.

### 5. Ion Exchange

Ion exchangers exchange one ion for another, hold it temporarily, and then release it to a regenerant solution. In an ion-exchange system, undesirable ions in the water supply are replaced with more acceptable ions.

Ionizable groups attached to the resin bead determine the functional capability of the resin. Industrial water treatment resins are classified into four basic categories: strong acid cation (SAC); weak acid cation (WAC); strong base anion (SBA); and weak base anion (WBA).

SAC resins can neutralize strong bases and convert neutral salts into their corresponding acids. SBA resins can neutralize strong acids and convert neutral salts into their corresponding bases. These resins are used in most softening and full demineralization applications. WAC and WBA resins are able to neutralize strong bases and acids, respectively. These resins are used for dealkalization, partial demineralization, or (in combination with strong resins) full demineralization.

#### 5.1. Sodium Zeolite Softening

Sodium zeolite softening is the most widely applied use of ion exchange. In zeolite softening, water containing scale-forming ions, such as calcium and magnesium, passes through a resin bed containing SAC resin in the sodium form. In the resin, the hardness ions are exchanged with the sodium, and the sodium diffuses into the bulk water solution. The hardness-free water, termed soft water, can then be used for low to medium pressure boiler feedwater, reverse osmosis system makeup, some chemical processes, and commercial applications, such as laundries.

#### 5.2. Demineralization

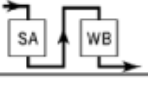
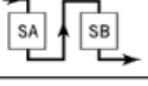

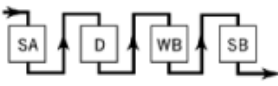
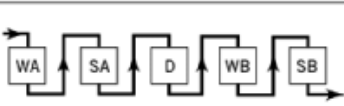
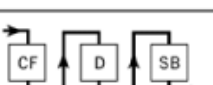
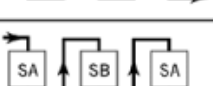


Softening alone is insufficient for most high-pressure boiler feed waters and for many process streams, especially those used in the manufacture of electronics equipment. In addition to the removal of hardness, these processes require removal of all dissolved solids, such as sodium, silica, alkalinity, and the mineral anions ( $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{NO}_3^-$ ).

Demineralization of water is the removal of essentially all inorganic salts by ion exchange. In this process, strong acid cation resin in the hydrogen form converts dissolved salts into their corresponding acids, and strong base anion resin in the hydroxide form removes these acids. Demineralization produces water similar in quality to distillation at a lower cost for most fresh waters.

The standard cation–anion process has been modified in many systems to reduce the use of costly regenerants and the production of waste. Modifications include the use of decarbonators, weak acid and weak base resins. Several different approaches to demineralization using these processes are shown in Figure 1.

#### 5.3. Condensate Polishing

Ion exchange can be used to purify or polish returned condensate, removing corrosion products that could cause harmful deposits in boilers. Typically, the contaminants in the condensate system are particulate iron and copper. Low levels of other contaminants may enter the system through condenser and pump seal leaks or

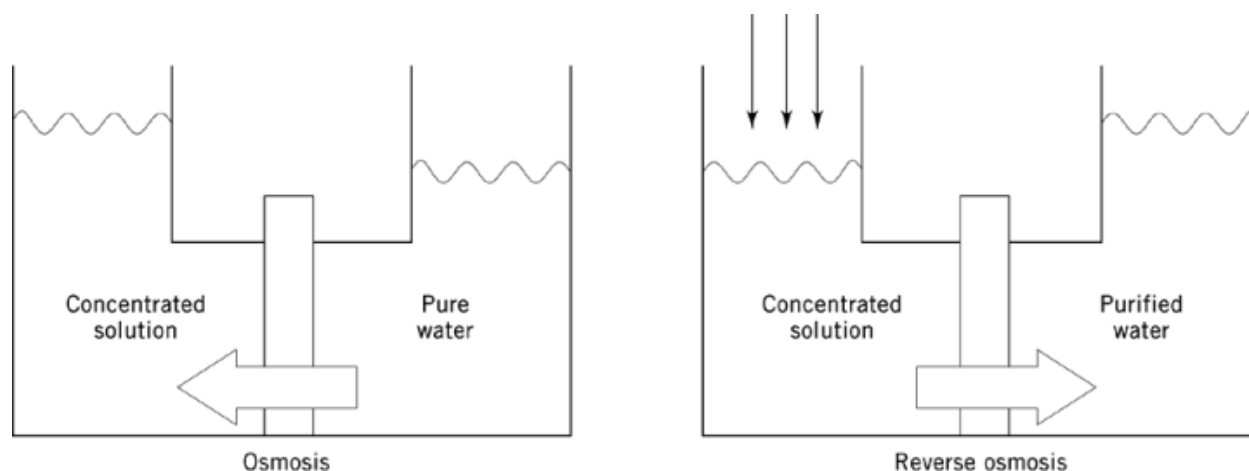
System	Application	Typical Effluent	Advantages and Limitations
	Silica and CO <sub>2</sub> are not objectionable	Conductance: 10–40 intro silica unchanged	Low equipment costs low regenerant costs
	Lower alkalinity, raw water, silica, and CO <sub>2</sub> removal required	Conductance: <15 intro silica: 0.02–0.10 ppm	Low equipment costs Medium regenerant costs
	High alkalinity, raw water, silica, and CO <sub>2</sub> removal required	Conductance: <15 intro silica: 0.02–0.10 ppm	Low regenerant costs Repumping required
	High alkalinity, chloride and sulfate, raw water, silica, and CO <sub>2</sub> removal required	Conductance: <15 intro silica: 0.02–0.10 ppm	Higher equipment cost lowest regenerant cost repumping required
	High hardness, alkalinity, chloride, and sulfate, raw water, silica, and CO <sub>2</sub> removal required	Conductance: <10 intro silica: 0.02–0.06 ppm	Higher equipment cost lowest regenerant cost repumping required
	High sodium, raw water, low leakage required	Conductance: <10 intro silica: 0.02–0.06 ppm	Medium equipment cost lower acid cost for leakage obtained
	High sodium, raw water, existing 2-bed system, low leakage required	Conductance: <5 intro silica: 0.02–0.06 ppm	Easy to retrofit system danger of acidic water on anion breakthrough
	Low solids, raw water, high purity required	Conductance: <1 intro silica: 0.01–0.05 ppm	Low equipment cost high chemical cost, higher attention required
	High solids, water, high purity required	Conductance: <1 intro silica: 0.01–0.05 ppm	Medium equipment cost high chemical cost, higher attention required

**Fig. 1.** Demineralizer systems consist of various unit processes arranged to meet the system needs. **SA** Strong acid cation exchanger; **SB** Strong base anion exchanger; **D** Degasifier; **MB** Mixed bed; **WA** Weak acid cation exchanger; **WB** Weak base anion exchanger; and **CF** Counterflow cation.

carryover of boiler water into the steam. Condensate polishers filter out the particulates and remove soluble contaminants by ion exchange.

Most paper mill condensate polishers operate at temperatures approaching 93°C, precluding the use of anion resin. Cation resin, which is stable up to temperatures of over 132°C, is used for deep bed condensate polishing in these applications. The resin is regenerated with sodium chloride brine, as in a zeolite softener. In situations in which sodium leakage from the polisher adversely affects the boiler water internal chemical program or steam attenuating water purity, the resin can be regenerated with an ionized amine solution to prevent these problems.

## 8 WATER, INDUSTRIAL WATER TREATMENT



**Fig. 2.** In the osmosis process, water flows through a membrane from a dilute solution to a more concentrated solution. In reverse osmosis, applied pressure causes water to flow in the opposite direction.

### 6. Membrane Processes

In recent years, membrane processes have been used increasingly for the production of “pure” waters from fresh water and seawater. Membrane processes are also being applied in process and wastewater systems. Although often thought to be expensive and relatively experimental, membrane technology is advancing quickly, becoming less expensive, improving performance, and extending life expectancy.

Common membrane processes include ultrafiltration (UF), reverse osmosis (RO), electrodialysis (ED), and electrodialysis reversal (EDR). These processes (with the exception of UF) remove most ions; RO and UF systems also provide efficient removal of nonionized organics and particulates. Because UF membrane porosity is too large for ion rejection, the UF process is used to remove contaminants, such as oil and grease, and suspended solids.

#### 6.1. Reverse Osmosis

Osmosis is the flow of solvent through a semipermeable membrane, from a dilute solution to a concentrated solution. This flow results from the driving force created by the difference in pressure between the two solutions. Osmotic pressure is the pressure that must be added to the concentrated solution side to stop the solvent flow through the membrane. Reverse osmosis is the process of reversing the flow, forcing water through a membrane from a concentrated solution to a dilute solution to produce pure water. Figure 2 illustrates the processes of osmosis and reverse osmosis.

Reverse osmosis is created when sufficient pressure is applied to the concentrated solution to overcome the osmotic pressure. This pressure is provided by feed-water pumps. Concentrated contaminants (brine) are removed from the high pressure side of the RO membrane, and pure water (permeate) is removed from the low pressure side. Membrane modules may be staged in various design configurations, producing the highest quality permeate with the least amount of waste.

Typically, 95% of dissolved salts are removed from the brine. All particulates are removed. However, due to their molecular porosity, RO membranes do not remove dissolved gases, such as  $\text{Cl}_2$ ,  $\text{CO}_2$ , and  $\text{O}_2$ .



## 6.2. Electrodialysis

Electrodialysis processes transfer ions of dissolved salts across membranes, leaving purified water behind. Ion movement is induced by direct current electrical fields. A negative electrode (cathode) attracts cations, and a positive electrode (anode) attracts anions. Systems are compartmentalized in stacks by alternating cation and anion transfer membranes. Alternating compartments carry concentrated brine and purified permeate. Typically, 40–60% of dissolved ions are removed or rejected. Further improvement in water quality is obtained by staging (operation of stacks in series). ED processes do not remove particulate contaminants or weakly ionized contaminants, such as silica.

## 6.3. Electrodialysis Reversal

Electrodialysis reversal processes operate on the same principles as ED; however, EDR operation reverses system polarity (typically three to four times per hour). This reversal stops the buildup of concentrated solutions on the membrane and thereby reduces the accumulation of inorganic and organic deposition on the membrane surface. EDR systems are similar to ED systems, designed with adequate chamber area to collect both product water and brine. EDR produces water of the same purity as ED.

# 7. Boilers

## 7.1. Boiler System Corrosion

The dissolved gases normally present in water cause many corrosion problems. For instance, oxygen in water produces pitting that is particularly severe because of its localized nature (Fig. 3). Carbon dioxide corrosion is frequently encountered in condensate systems and less commonly in water distribution systems. Water containing ammonia, particularly in the presence of oxygen, readily attacks copper and copper-bearing alloys. The resulting corrosion leads to deposits on boiler heat transfer surfaces and reduces efficiency and reliability. In addition to the gases, corrosion can also be caused by the concentration of caustic or acidic species in the feed water.

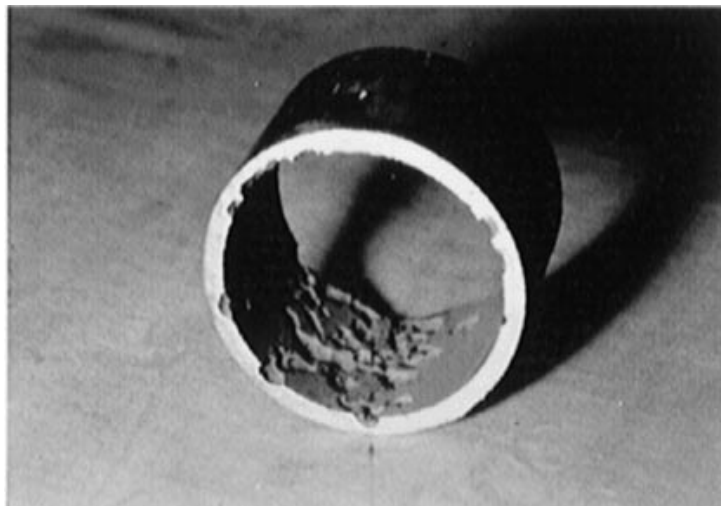
### 7.1.1. Caustic Corrosion

Concentration of caustic (NaOH) can occur either as a result of steam blanketing (which allows salts to concentrate on boiler metal surfaces) or by localized boiling beneath porous deposits on tube surfaces.

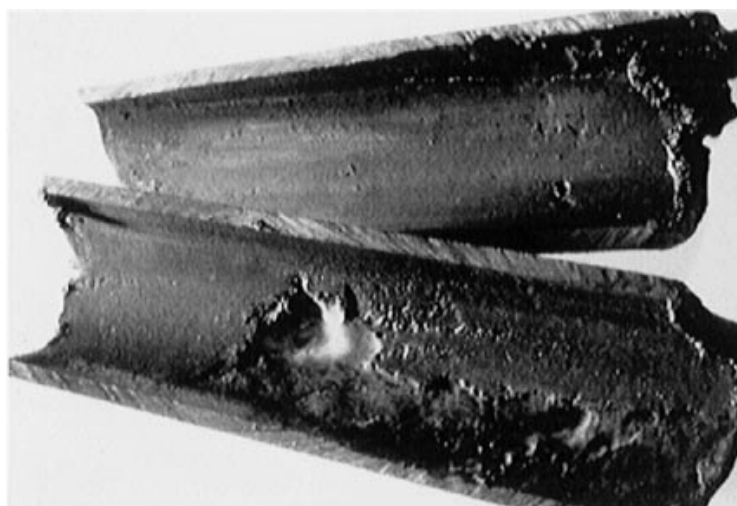
Caustic corrosion (gouging) occurs when caustic is concentrated and dissolves the protective magnetite ( $\text{Fe}_3\text{O}_4$ ) layer. Iron, in contact with the boiler water, forms magnetite and the protective layer is continuously restored. However, as long as a high caustic concentration exists, the magnetite is constantly dissolved, causing a loss of base metal and eventual failure (Fig. 4).

Steam blanketing is a condition that occurs when a steam layer forms between the boiler water and the tube wall. Under this condition, insufficient water reaches the tube surface for efficient heat transfer. The water that does reach the overheated boiler wall is rapidly vaporized, leaving behind a concentrated caustic solution, which is corrosive.

Porous metal oxide deposits also permit the development of high boiler water concentrations. Water flows into the deposit and heat applied to the tube causes the water to evaporate, leaving a concentrated solution. Again, corrosion may occur. Caustic attack creates irregular patterns, often referred to as gouges. Deposition may or may not be found in the affected area.



**Fig. 3.** Tube severely damaged by oxygen.



**Fig. 4.** Caustic gouging caused failure of this boiler tube.

#### **7.1.2. Acidic Corrosion**

Low makeup or feed-water pH can cause serious acid attack on metal surfaces in the preboiler and boiler system. Even if the original makeup or feed-water pH is not low, feed water can become acidic from contamination of the system. Common causes include improper operation or control of demineralizer cation units, process contamination of condensate (eg, sugar contamination in food processing plants), and cooling water contamination from condensers. Acid corrosion can also be caused by chemical cleaning operations. Overheating of the cleaning solution can cause breakdown of the inhibitor used, excessive exposure of metal to cleaning agent, and high cleaning agent concentration. Failure to neutralize acid solvents completely before startup has also caused problems. In a boiler and feed-water system, acidic attack can take the form of general thinning, or it can be localized at areas of high stress such as drum baffles, U bolts, acorn nuts, and tube ends.

### 7.1.3. Hydrogen Embrittlement

Hydrogen embrittlement is rarely encountered in industrial plants. The problem usually occurs only in boilers operating at or above  $689.5 \times 10^3$  Pa. Hydrogen embrittlement of mild steel boiler tubing occurs in high pressure boilers when atomic hydrogen forms at the boiler tube surface as a result of corrosion. Hydrogen permeates the tube metal, where it can react with iron carbides to form methane gas, or with other hydrogen atoms to form hydrogen gas. These gases evolve predominantly along grain boundaries of the metal. The resulting increase in pressure leads to metal failure.

The initial surface corrosion that produces hydrogen usually occurs beneath a hard, dense scale. Acidic contamination or localized low pH excursions are normally required to generate atomic hydrogen. In high purity systems, raw water in-leakage (eg, condenser leakage) lowers boiler water pH when magnesium hydroxide precipitates, resulting in corrosion, formation of atomic hydrogen, and initiation of hydrogen attack.

### 7.1.4. Stress Corrosion Cracking

Stress corrosion cracking occurs from the combined action of corrosion and stress. The corrosion may be initiated by improper chemical cleaning, high dissolved oxygen levels, pH excursions in the boiler water, the presence of free hydroxide, and high levels of chlorides. Stresses are either residual in the metal or caused by thermal excursions. Rapid startup or shutdown can cause or further aggravate stresses. Tube failures occur near stressed areas such as welds, supports, or cold worked areas.

## 7.2. Boiler Deposits

Deposition is a principal problem in the operation of steam generating equipment. The accumulation of material on boiler surfaces can cause overheating and/or corrosion. Both of these conditions frequently result in unscheduled downtime. Common feed-water contaminants that can form boiler deposits include calcium, magnesium, iron, copper, aluminum, silica, and (to a lesser extent) silt and oil. Most deposits can be classified as one of two types: scale that crystallized directly onto tube surfaces or sludge deposits that precipitated elsewhere and were transported to the metal surface by the flowing water.

Boiler feed water pretreatment systems have advanced to such an extent that it is now possible to provide boilers with ultrapure water. However, this degree of purification requires the use of elaborate pretreatment systems. The capital expenditures for such pretreatment equipment trains can be considerable and are often not justified when balanced against the capability of internal treatment.

The quality of feed water required depends on boiler operating pressure, design, heat transfer rates, and steam use. Most boiler systems have sodium zeolite softened or demineralized makeup water. Feed-water hardness usually ranges from 0.01 to 2.0 ppm, but even water of this purity does not provide deposit-free operation. Therefore, good internal boiler water treatment programs are necessary.

## 7.3. Boiler Water Treatment

### 7.3.1. Oxygen Control

To meet industrial standards for both oxygen content and the allowable metal oxide levels in feed water, nearly complete oxygen removal is required. This can be accomplished only by efficient mechanical deaeration supplemented by an effective and properly controlled chemical oxygen scavenger.

To deaerate the boiler feedwater, water is sprayed into a steam atmosphere. This heats the water to within a few degrees of the temperature of the saturated steam. Because the solubility of oxygen in water is low under these conditions, 97–98% of the oxygen in the incoming water is released to the steam and is purged from the system by venting. Although the remaining oxygen is not soluble under equilibrium conditions, it is not readily released to the steam. Therefore, water leaving the heating section of the deaerator must be scrubbed vigorously with steam to maximize removal.

## 12 WATER, INDUSTRIAL WATER TREATMENT

In addition to mechanical deaeration, chemical oxygen scavengers are used to remove any remaining oxygen. The oxygen scavengers most commonly used in boiler systems are sodium sulfite, sodium bisulfite, hydrazine, catalyzed versions of the sulfites and hydrazine, and organic oxygen scavengers, such as hydroquinone and ascorbate.

It is of critical importance to select and properly use the best chemical oxygen scavenger for a given system. Principal factors that determine the best oxygen scavenger for a particular application include reaction speed, residence time in the system, operating temperature and pressure, and feed-water pH. Interferences with the scavenger–oxygen reaction, decomposition products, and reactions with metals in the system are also important factors. Other contributing factors include the use of feed water for attemperation, the presence of economizers in the system, and the end use of the steam. Chemical oxygen scavengers should be fed to allow ample time for the scavenger–oxygen reaction to occur. The deaerator storage system and the feed-water storage tank are commonly used feed points.

Scale and deposits are controlled through the use of phosphates, chelants, and polymers. Phosphates are precipitating treatments, and chelants are solubilizing treatments. Polymers are most widely used to disperse particulates but they are also used to solubilize contaminants under certain conditions.

### **7.3.2. Phosphate Treatment**

Calcium phosphate is virtually insoluble in boiler water. Even small levels of phosphate can be maintained to ensure the precipitation of calcium phosphate in the bulk boiler water, away from heating surfaces. Therefore, the introduction of phosphate treatment eliminates the formation of calcium carbonate scale on tube surfaces. When calcium phosphate is formed in boiler water of sufficient alkalinity, a particle with a relatively nonadherent surface charge is produced. This does not prevent the development of deposit accumulations over time, but the deposits can be controlled reasonably well by blowdown.

In a phosphate precipitation treatment program, the magnesium portion of the hardness contamination is precipitated preferentially as magnesium silicate. If silica is not present, the magnesium will precipitate as magnesium hydroxide. If insufficient boiler water hydroxide is being maintained, magnesium can combine with phosphate. Magnesium phosphate has a surface charge that can cause it to adhere to tube surfaces and then collect other solids. For this reason, alkalinity is an important part of a phosphate precipitation program.

### **7.3.3. Phosphate–Polymer Control**

Phosphate treatment results are improved by organic supplements. Naturally occurring organics such as lignins, tannins, and starches were the first supplements used. The organics were added to promote the formation of a fluid sludge that would settle in the mud drum. Bottom blowdown from the mud drum removed the sludge.

There have been many advances in organic treatments. Synthetic polymers are now used widely, and the emphasis is on dispersion of particles rather than fluid sludge formation. Although this mechanism is quite complex, polymers alter the surface area and the surface charge to mass ratio of the boiler solids. Many synthetic polymers are used in phosphate precipitation programs. Most are effective in dispersing magnesium silicate and magnesium hydroxide as well as calcium phosphate. The polymers are usually low in molecular weight and have numerous active sites. Some polymers are used specifically for hardness salts or for iron; some are effective for a broad spectrum of ions.

### **7.3.4. Chelant Control**

Chelants are the prime additives in a solubilizing boiler water treatment program. Chelants have the ability to complex many cations (hardness and heavy metals under boiler water conditions). They accomplish this by locking metals into a soluble organic ring structure. The chelated cations do not deposit in the boiler. When applied with a dispersant, chelants produce clean waterside surfaces.

### 7.3.5. Chelant–Polymer Control

Iron oxide is of particular concern in today's boiler water treatment programs. Deposition from low (less than 1.0 ppm) hardness boiler feed water is eliminated with chelant programs and can be reduced by up to 95% by a good polymer–phosphate treatment program. Iron oxide is an increasingly significant contributor to boiler deposits, because of the virtual elimination of hardness deposits in many systems and because the high heat transfer rates of many boilers encourage iron deposition.

A chelant–polymer combination is an effective approach to controlling iron oxide. Adequate chelant is fed to complex hardness and soluble iron, with a slight excess to solubilize iron contamination. Polymers are then added to condition and disperse any remaining iron oxide contamination.

A chelant–polymer program can produce clean waterside surfaces, contributing to much more reliable boiler operation. Out-of-service boiler cleaning schedules can be extended and, in some cases, eliminated. This depends on operational control and feed-water quality. Chelants with high complexing stabilities are “forgiving” treatments; they can remove deposits that form when feed-water quality or treatment control periodically deviates from standard.

### 7.3.6. Phosphate–Chelant–Polymer Combinations

Combinations of polymer, phosphate, and chelant are commonly used to produce results comparable to chelant–polymer treatment in boilers operating at  $4137 \times 10^3$  Pa or less. Boiler cleanliness is improved over phosphate treatment, and the presence of phosphate provides an easy means of testing to confirm the presence of treatment in the boiler water.

### 7.3.7. Polymer-only Treatment

Polymer-only treatment programs are also used with a degree of success. In this treatment, the polymer is usually used as a weak chelant to complex the feed-water hardness. These treatments are most successful when feed-water hardness is consistently low.

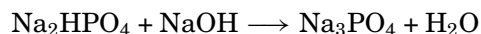
### 7.3.8. High Pressure Boiler Water Treatment

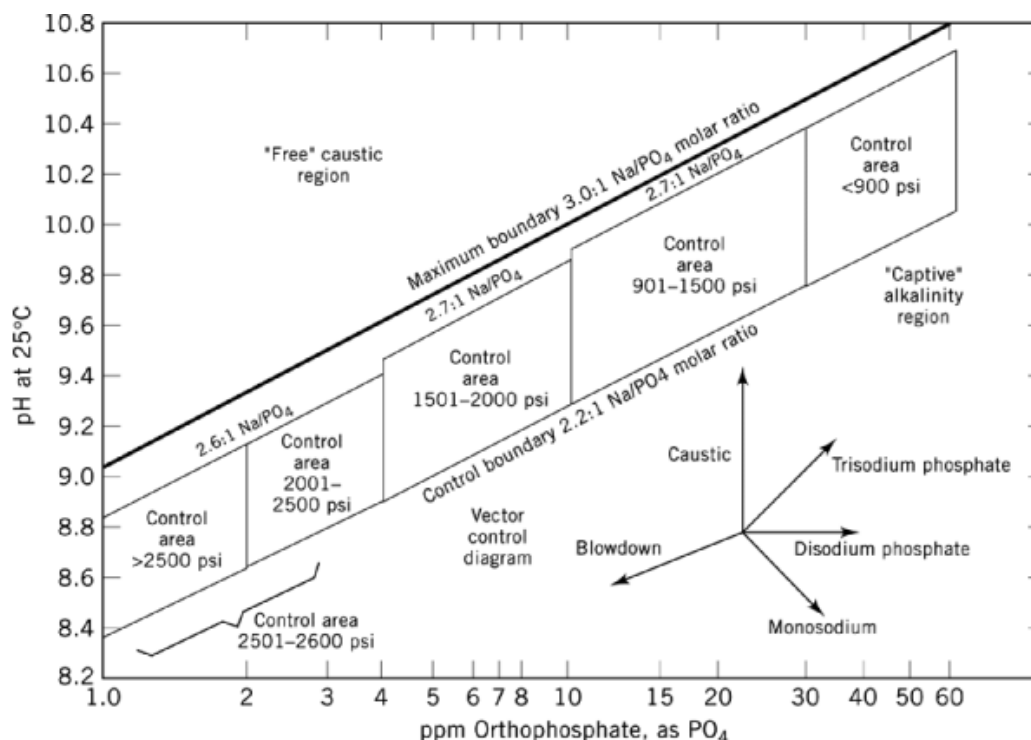
High pressure boilers usually have feed water composed of demineralized makeup water and a high percentage of condensate returns. Because of these conditions, high pressure boilers are prone to caustic and acid attack. Low pressure boilers that use demineralized water and condensate as feed water are also susceptible to caustic and acid attack.

There are several means by which boiler water can become highly concentrated. One of the most common is iron oxide deposition on radiant wall tubes. Iron oxide deposits are often quite porous and act as miniature boilers. Water is drawn into the iron oxide deposit. Heat applied to the deposit from the tube wall generates steam, which passes out through the deposit. More water enters the deposit, taking the place of the steam. This cycle is repeated and the water beneath the deposit is concentrated to extremely high levels. It is possible to have 100,000 ppm of caustic beneath the deposit while the bulk water contains only about 5–10 ppm of caustic.

Boiler feed-water systems that use demineralized or evaporated makeup or pure condensate may be protected from caustic attack through coordinated phosphate and pH control. Phosphate buffers the boiler water, reducing the chance of large pH changes due to the development of high caustic or acid concentrations. Excess caustic combines with disodium phosphate and forms trisodium phosphate. Sufficient disodium phosphate must be available to combine with all of the free caustic in order to form trisodium phosphate.

Disodium phosphate neutralizes caustic by the following reaction:

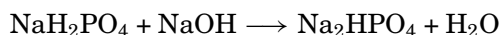




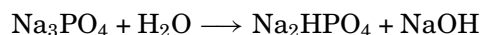
**Fig. 5.** Coordinated phosphate–pH control avoids both acid and caustic corrosion. To convert psi to kPa, divide by 6.895.

This results in the prevention of caustic buildup beneath deposits or within a crevice where leakage is occurring. Caustic corrosion (and caustic embrittlement, discussed later) does not occur, because high caustic concentrations do not develop.

Figure 5 shows the phosphate–pH relationship recommended to control boiler corrosion. Different forms of phosphate consume or add caustic as the phosphate shifts to the proper form. For example, addition of monosodium phosphate consumes caustic as it reacts with caustic to form disodium phosphate in the boiler water according to the following reaction:

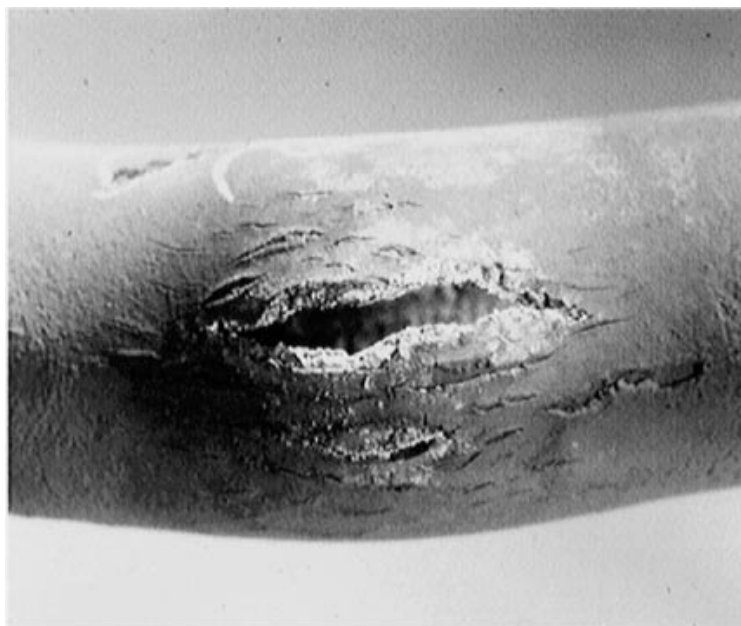


Conversely, addition of trisodium phosphate adds caustic, increasing boiler water pH:



Control is achieved through feed of the proper type of phosphate either to raise or to lower the pH while maintaining the proper phosphate level. Increasing blowdown lowers both phosphate and pH. Therefore, various combinations and feedrates of phosphate, blowdown adjustment, and caustic addition are used to maintain proper phosphate–pH levels.

Elevated temperatures at the boiler tube wall or deposits can result in some precipitation of phosphate. This effect, termed *phosphate hideout*, usually occurs when loads increase. When the load is reduced, phosphate reappears.



**Fig. 6.** Boiler water contamination of the steam caused superheater deposits, which led to tube metal overheating and failure.

Clean boiler water surfaces reduce potential concentration sites for caustic. Deposit control treatment programs, such as those based on chelants and synthetic polymers, can help provide clean surfaces.

When steam blanketing is occurring, corrosion can take place even without the presence of caustic, due to the steam–magnetite reaction and the dissolution of magnetite. In such cases, operational changes or design modifications may be necessary to eliminate the cause of the problem.

If deposits are minimized, the areas where caustic can be concentrated is reduced. To minimize the iron deposition in  $6.895 - 12.07 \times 10^6$  Pa boilers, specific polymers have been designed to disperse the iron and keep it in the bulk water. As with phosphate precipitation and chelant control programs, the use of these polymers with coordinated phosphate–pH treatment improves deposit control.

Supercritical boilers use all-volatile treatments, generally consisting of ammonia and hydrazine. Because of the extreme potential for deposit formation and steam contamination, no solids can be tolerated in supercritical once-through boiler water, including treatment solids.

#### 7.4. Steam Purity

Boiler water solids carried over with steam form deposits in nonreturn valves, superheaters, and turbine stop and control valves. Carryover can contaminate process streams and affect product quality. Deposition in superheaters can lead to failure due to overheating and corrosion, as shown in Figure 6.

Superheated steam turbines are particularly prone to damage by carryover. Sticking of governor and stop valves due to deposits can cause turbine overspeed and catastrophic damage. Solid particles in steam can erode turbine parts, while deposition on turbine blades can reduce efficiency and capacity. Losses of 5% in turbine efficiency and 20% in turbine capacity have occurred due to deposition. When large slugs of boiler water carry over with steam, the resulting thermal and mechanical shock can cause severe damage.

## 16 WATER, INDUSTRIAL WATER TREATMENT

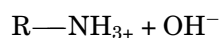
Steam can be contaminated with solids even when carryover is not occurring. Contaminated spray attemperating water, used to control superheated steam temperature at the turbine inlet, can introduce solids into steam. A heat exchanger coil may be placed in the boiler mud drum to provide attemperation of the superheated steam. Because the mud drum is at a higher pressure than superheated steam, contamination will occur if leaks develop in the coil.

### 8. Chemical Treatment of Condensate Systems

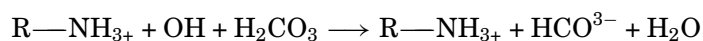
Condensate systems can be chemically treated to reduce metal corrosion. Treatment chemicals include neutralizing amines, filming amines, and oxygen scavenger-metal passivators.

#### 8.1. Neutralizing Amines

Neutralizing amines are used to neutralize the acid ( $\text{H}^+$ ) generated by the dissolution of carbon dioxide or other acidic process contaminants in the condensate. These amines hydrolyze when added to water and generate the hydroxide ions required for neutralization:



The overall neutralization reaction can be written as shown:



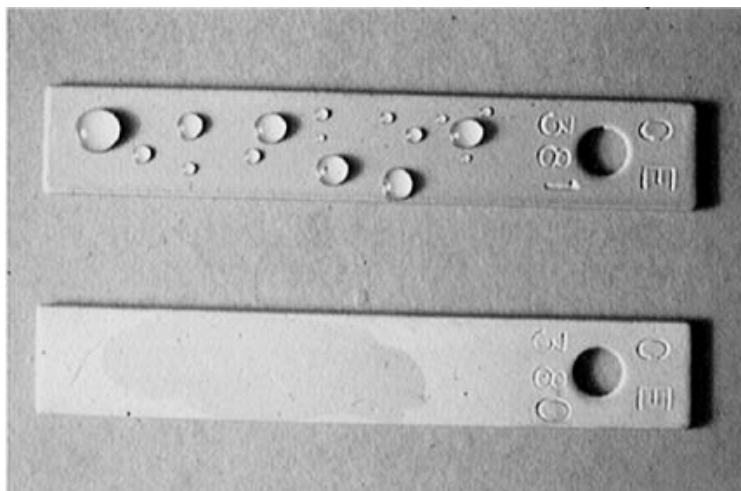
By regulating the neutralizing amine feed rate, the condensate pH can be elevated to within a desired range (eg, 8.8–9.2 for a mixed copper–iron condensate system).

#### 8.2. Filming Amines

Another approach to controlling condensate system corrosion is the use of chemicals that form a protective film on metal surfaces (Fig. 7). This approach has come into widespread use with the development of suitable products containing long-chain nitrogenous materials. Filming amines protect against oxygen and carbon dioxide corrosion by replacing the loose oxide scale on metal surfaces with a thin amine film barrier.

Advances have been made in formulating filming amine treatments. Straight filming amines containing one ingredient, such as octadecylamine, are effective but often fail to cover the entire system and can produce fouling. Emulsifiers and, in some cases, small amounts of neutralizing amines can be added to improve film distribution by providing more uniform coverage. This increases system protection and reduces the fouling potential. Application experience has shown that combination amines (filming and neutralizing amines with dispersant aids) provide a superior film bond, reduce deposit problems, and provide better system coverage and thus provide more complete and economical corrosion protection.





**Fig. 7.** Test specimens illustrate the nonwetttable surface produced by a filming amine (381) compared with an untreated surface (380).

### 8.3. Oxygen Scavenging and Metal Passivation

Where oxygen invades the condensate system, corrosion of iron and copper-bearing components can be overcome through proper pH control and the injection of an oxygen scavenger. One important factor to consider in choosing an oxygen scavenger for condensate treatment is its reactivity with oxygen at the temperature and pH of the system. A scavenger that removes oxygen rapidly provides the best protection for the condensate metallurgy. Hydroquinone has been shown to be particularly effective for most systems.

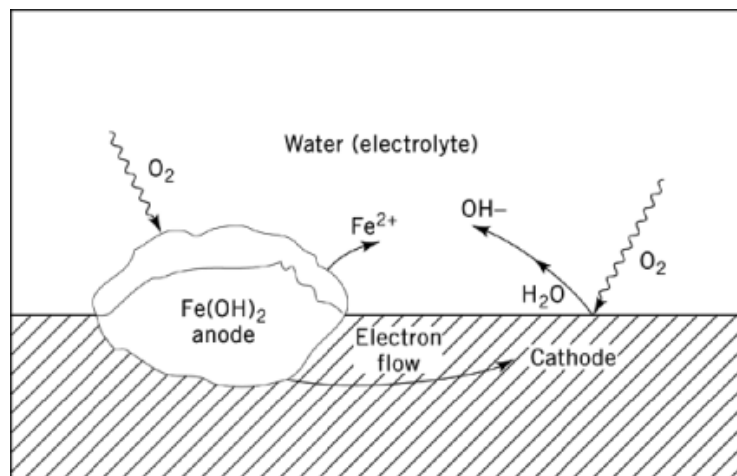
The use of neutralizing amines in conjunction with an oxygen scavenger-metal passivator improves corrosion control in two ways. First, because any acidic species present is neutralized and pH is increased, the condensate becomes less corrosive. Second, most oxygen scavenger-passivators react more rapidly at the mildly alkaline conditions maintained by the amine than at lower pH levels. For these reasons, this combination treatment is gaining wide acceptance, particularly for the treatment of condensate systems that are contaminated by oxygen.

## 9. Cooling Systems

### 9.1. Cooling System Corrosion

Corrosion can be defined as the destruction of a metal by chemical or electrochemical reaction with its environment. In cooling systems, corrosion causes two basic problems. The first and most obvious is the failure of equipment with the resultant cost of replacement and plant downtime. The second is decreased plant efficiency to loss of heat transfer, the result of heat exchanger fouling caused by the accumulation of corrosion products.

Corrosion occurs at the anode, where metal dissolves. Often, this is separated by a physical distance from the cathode, where a reduction reaction takes place. An electrical potential difference exists between these sites, and current flows through the solution from the anode to the cathode. This is accompanied by the flow of electrons from the anode to the cathode through the metal (Fig. 8).

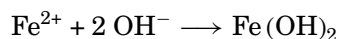


**Fig. 8.** A corrosion cell.

For steel, the typical anodic oxidation reaction is

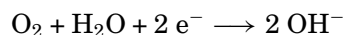


This reaction is accompanied by the following:



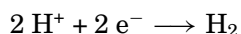
The ferrous hydroxide then combines with oxygen and water to produce ferric hydroxide,  $\text{Fe(OH)}_3$ , which becomes common iron rust when dehydrated to  $\text{Fe}_2\text{O}_3$ .

The primary cathodic reaction in cooling systems is

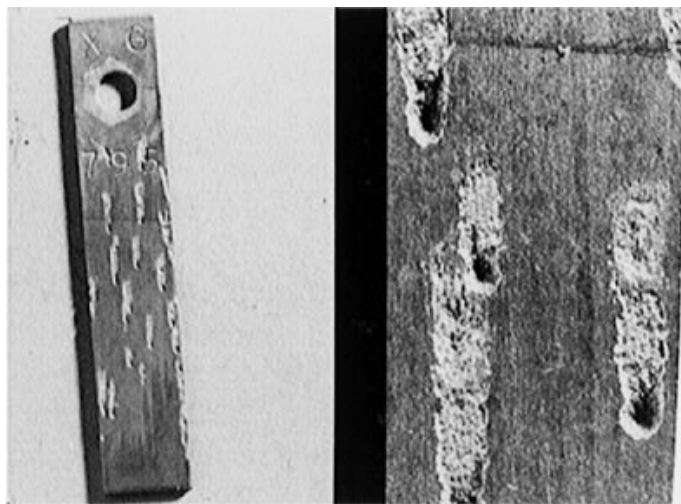


The production of hydroxide ions creates a localized high pH at the cathode, approximately 1–2 pH units above bulk water pH. Dissolved oxygen reaches the surface by diffusion, as indicated by the wavy lines in Figure 8. The oxygen reduction reaction controls the rate of corrosion in cooling systems; the rate of oxygen diffusion is usually the limiting factor.

Another important cathodic reaction is



At neutral or higher pH, the concentration of  $\text{H}^{+}$  ions is too low for this reaction to contribute significantly to the overall corrosion rate. However, as pH decreases, this reaction becomes more important until, at a pH of about 4, it becomes the predominant cathodic reaction.



**Fig. 9.** Pitting corrosion is damaging because it can lead rapidly to equipment failure.

## 10. Types of Corrosion

The formation of anodic and cathodic sites, necessary to produce corrosion, can occur for any of a number of reasons: impurities in the metal, localized stresses, metal grain size or composition differences, discontinuities on the surface, and differences in the local environment (eg, temperature, oxygen, or salt concentration). When these local differences are not large and the anodic and cathodic sites can shift from place to place on the metal surface, corrosion is uniform. With uniform corrosion, fouling is usually a more serious problem than equipment failure.

Localized corrosion, which occurs when the anodic sites remain stationary, is a more serious industrial problem. Forms of localized corrosion include pitting, selective leaching (eg, dezincification), galvanic corrosion, crevice or underdeposit corrosion, intergranular corrosion, stress corrosion cracking, and microbiologically influenced corrosion. Another form of corrosion, which cannot be accurately categorized as either uniform or localized, is erosion corrosion.

### 10.1. Pitting

Pitting is one of the most destructive forms of corrosion and also one of the most difficult to predict in laboratory tests (Fig. 9). Pitting occurs when anodic and cathodic sites become stationary due to large differences in surface conditions. It is generally promoted by low velocity or stagnant conditions (eg, shellside cooling) and by the presence of chloride ions. Once a pit is formed, the solution inside it is isolated from the bulk environment and becomes increasingly corrosive. The high corrosion rate in the pit produces an excess of positively charged metal cations, which attract chloride anions. In addition, hydrolysis produces  $H^+$  ions. The increase in acidity and concentration within the pit promotes even higher corrosion rates, and the process becomes self-sustaining. Inhibitors can be used to control pitting, but they must be applied correctly.

### 10.2. Selective Leaching

Selective leaching is the corrosion of one element of an alloy. The most common example in cooling systems is dezincification, which is the selective removal of zinc from copper–zinc alloys. The conditions that promote the

**Table 4. Galvanic Series of Metals and Alloys<sup>a</sup>**

Corroded End (anodic, or least noble)	
magnesium	Inconel (active)
magnesium alloys	Hastelloy A
zinc	Hastelloy B
Aluminum 2S	brasses
cadmium	copper
Aluminum 17ST	bronzes
steel or iron	copper–nickel alloys
cast iron	titanium
chromium–iron (active)	Monel
Ni-Resist	silver solder
18-8-Cr-Ni-Fe (active)	nickel (passive)
15-8-3'-Cr-Ni-Mo-Fe (active)	Inconel (passive)
Hastelloy C	chromium–iron (passive)
lead–tin solders	18-8 Cr-Ni-Fe (passive)
lead	18-8-3 Cr-Ni-Mo-Fe (passive)
tin	silver
nickel (active)	graphite
Protected End (cathodic, or most noble)	

<sup>a</sup>Courtesy of International Nickel Company, Inc.

pitting of steel also promote the pitting of brass, which in cooling systems usually occurs by dezincification. Low pH conditions ( $<6.0$ ) and high free chlorine residuals ( $<1.0$  ppm) are particularly aggressive in producing dezincification. The dezincification resistance varies with the alloy. For example, 70–30 brass is less resistant than Admiralty brass (70–30 brass plus 1% tin), which is less resistant than inhibited Admiralty brass (Admiralty brass plus a small amount of arsenic, antimony, or phosphorus).

### 10.3. Galvanic Corrosion

Galvanic corrosion occurs when two dissimilar metals are in contact in a solution. The contact must be good enough to conduct electricity, and both metals must be exposed to the solution. The driving force for galvanic corrosion is the electric potential difference that develops between two metals. This difference increases as the distance between the metals in the galvanic series increases.

Table 4 shows a galvanic series for some commercial metals and alloys. When two metals from the series are in contact in solution, the corrosion rate of the more active (anodic) metal increases and the corrosion rate of the more noble (cathodic) metal decreases.

Galvanic corrosion can be controlled by the use of sacrificial anodes. This is a common method of controlling corrosion in heat exchangers with Admiralty tube bundles and carbon steel tube sheets and channel heads. The anodes are bolted directly to the steel and protect a limited area around the anode. Proper placement of sacrificial anodes is a precise science.

The most serious form of galvanic corrosion occurs in cooling systems that contain both copper and steel alloys. It results when dissolved copper plates onto a steel surface and induces rapid galvanic attack of the steel. The amount of dissolved copper required to produce this effect is small and the increased corrosion is difficult to inhibit once it occurs. A copper corrosion inhibitor is needed to prevent copper dissolution.

### 10.4. Crevice Corrosion

Crevice corrosion is intense localized corrosion that occurs within a crevice or any area that is shielded from the bulk environment. Solutions within a crevice are similar to solutions within a pit in that they are highly

concentrated and acidic. Because the mechanisms of corrosion in the two processes are virtually identical, conditions that promote pitting also promote crevice corrosion. Alloys that depend on oxide films for protection (eg, stainless steel and aluminum) are highly susceptible to crevice attack because the films are destroyed by high chloride ion concentrations and low pH. This is also true of protective films induced by anodic inhibitors.

The best way to prevent crevice corrosion is to prevent crevices. From a cooling water standpoint, this requires the prevention of deposits on the metal surface. Deposits may be formed by suspended solids (eg, silt, silica) or by precipitating species, such as calcium salts.

### 10.5. Intergranular Corrosion

Intergranular corrosion is localized attack that occurs at metal grain boundaries. It is most prevalent in stainless steels that have been improperly heat treated. In these metals, the grain boundary area is depleted in chromium and, therefore, is less resistant to corrosion. Intergranular corrosion also occurs in certain high strength aluminum alloys. In general, it is not of significance in cooling systems.

### 10.6. Stress Corrosion Cracking

Stress corrosion cracking (SCC) is the brittle failure of a metal by cracking under tensile stress in a corrosive environment. Failures tend to be transgranular, although intergranular failures have been noted. Commonly used cooling system alloys that may crack due to stress include austenitic stainless steels (300 series) and brasses. The susceptibility of stainless steels to SCC increases significantly as the temperature is increased. Most laboratory stainless steel SCC testing is done at about 150°C, because it is difficult to promote cracking at temperatures below 93°C. For this reason, SCC of stainless steels has not been widely observed in cooling systems.

Chloride is the main contributor to SCC of stainless steels. High chloride concentrations, resulting from high chloride levels in the makeup water and/or high cycles of concentration, will increase susceptibility. Although low water temperatures generally preclude cracking, SCC of stainless steels can occur in cooling systems.

For brasses, the ammonium ion is the principal cause of SCC. Few service failures have been reported when ammonia is not present.

The most likely places for SCC to be initiated are crevices or areas where the flow of water is restricted. This is due to the buildup of corrodent concentrations in these areas. For example, chloride can concentrate from 100 ppm in the bulk water to as high as 10,000 ppm (1%) in a crevice. Deposits are initiating sites because of crevices formed beneath them. The low water velocities in shell-side cooling are also detrimental.

The most effective way to prevent SCC in both stainless steel and brass systems is to keep the system clean and free of deposits. An effective deposit control treatment is imperative. A good corrosion inhibitor is also beneficial. Chromate and phosphate have each been used successfully to prevent the SCC of stainless steel in chloride solutions.

### 10.7. Microbiologically Influenced Corrosion (MIC)

Microorganisms in cooling water form “biofilms” on cooling system surfaces. Biofilms consist of populations of sessile organisms and their hydrated polymeric secretions. Numerous types of organisms may exist in any particular biofilm, ranging from strictly aerobic bacteria at the water interface to anaerobic bacteria such as sulfate-reducing bacteria (SRB) at the oxygen-depleted metal surface. The presence of a biofilm can contribute to corrosion in three ways: physical deposition, production of corrosive by-products, and depolarization of the corrosion cell caused by chemical reactions.



**Fig. 10.** Microbiologically influenced corrosion (MIC).

As discussed above, deposits can cause accelerated localized corrosion by creating differential aeration cells. This same phenomenon occurs with a biofilm. The nonuniform nature of biofilm formation creates an inherent differential, which is enhanced by the oxygen consumption of organisms in the biofilm.

Many of the by-products of microbial metabolism, including organic acids and hydrogen sulfide, are corrosive. These materials can concentrate in the biofilm, causing accelerated metal attack. Corrosion tends to be self-limiting due to the buildup of corrosion reaction products. However, microbes can absorb some of these materials in their metabolism, thereby removing them from the anodic or cathodic site. The removal of reaction products, termed *depolarization*, stimulates further corrosion. Figure 10 shows a typical result of microbial corrosion. The surface exhibits scattered areas of localized corrosion, unrelated to flow pattern. The corrosion appears to spread in a somewhat circular pattern from the site of initial colonization.

#### 10.8. Erosion Corrosion

Erosion corrosion is the increase in the rate of metal deterioration from abrasive effects. It can be identified by grooves and rounded holes, which usually are smooth and have a directional pattern. Erosion corrosion is increased by high water velocities and suspended solids. It is often localized at areas where water changes direction. Cavitation (damage due to the formation and collapse of bubbles in high velocity turbines, propellers, etc) is a form of erosion corrosion. Its appearance is similar to closely spaced pits, although the surface is usually rough.

### 11. Control of Cooling System Corrosion

Corrosion control requires a change in either the metal or the environment. The first approach, changing the metal, is expensive. Also, highly alloyed materials, which are resistant to general corrosion, are more prone to failure by localized corrosion mechanisms such as stress corrosion cracking.

The second approach, changing the environment, is a widely used, practical method of preventing corrosion. In aqueous systems, there are three ways to effect a change in environment to inhibit corrosion: (1) form

a protective film of calcium carbonate on the metal surface using the natural calcium and alkalinity in the water, (2) remove the corrosive oxygen from the water, either by mechanical or chemical deaeration, and (3) add corrosion inhibitors.

### 11.1. Calcium Carbonate Protective Scale

The Langelier saturation index (LSI) is a useful tool for predicting the tendency of a water to deposit or dissolve calcium carbonate. Work published in 1936 deals with the conditions at which a water is in equilibrium with calcium carbonate. An equation developed by Langelier makes it possible to predict the tendency of calcium carbonate either to precipitate or to dissolve under varying conditions. The equation expresses the relationship of pH, calcium, total alkalinity, dissolved solids, and temperature as they relate to the solubility of calcium carbonate in waters with a pH of 6.5–9.5:

$$\text{pH}_s = (\text{p}K_2 - \text{p}K_s) + \text{pCa}^{2+} + \text{pAlk}$$

where  $\text{pH}_s$  is the pH at which water with a given calcium content and alkalinity is in equilibrium with calcium carbonate,  $K_2$  is the second dissociation constant for carbonic acid, and  $K_s$  is the solubility product constant for calcium carbonate. These terms are functions of temperature and total mineral content. Their values for any given condition can be computed from known thermodynamic constants. Both the calcium ion and the alkalinity terms are the negative logarithms of their respective concentrations. The calcium content is molar, while the alkalinity is an equivalent concentration (ie, the titratable equivalent of base per liter). The calculation of the  $\text{pH}_s$  has been simplified by the preparation of various nomographs. A typical one is shown in Figure 11.

The difference between the actual pH ( $\text{pH}_a$ ) of a sample of water and the  $\text{pH}_s$  ( $\text{pH}_a - \text{pH}_s$ ) is called the Langelier saturation index. This index is a qualitative indication of the tendency of calcium carbonate to deposit or dissolve. If the LSI is positive, calcium carbonate tends to deposit. If it is zero, the water is at equilibrium.

The LSI measures only the directional tendency or driving force for calcium carbonate to precipitate or dissolve. It cannot be used as a quantitative measure. Two different waters, one of low hardness (corrosive) and the other of high hardness (scale-forming), can have the same saturation index.

The stability index developed by Ryzner makes it possible to distinguish between two such waters. This index is based on a study of actual operating results with waters having various saturation indexes.

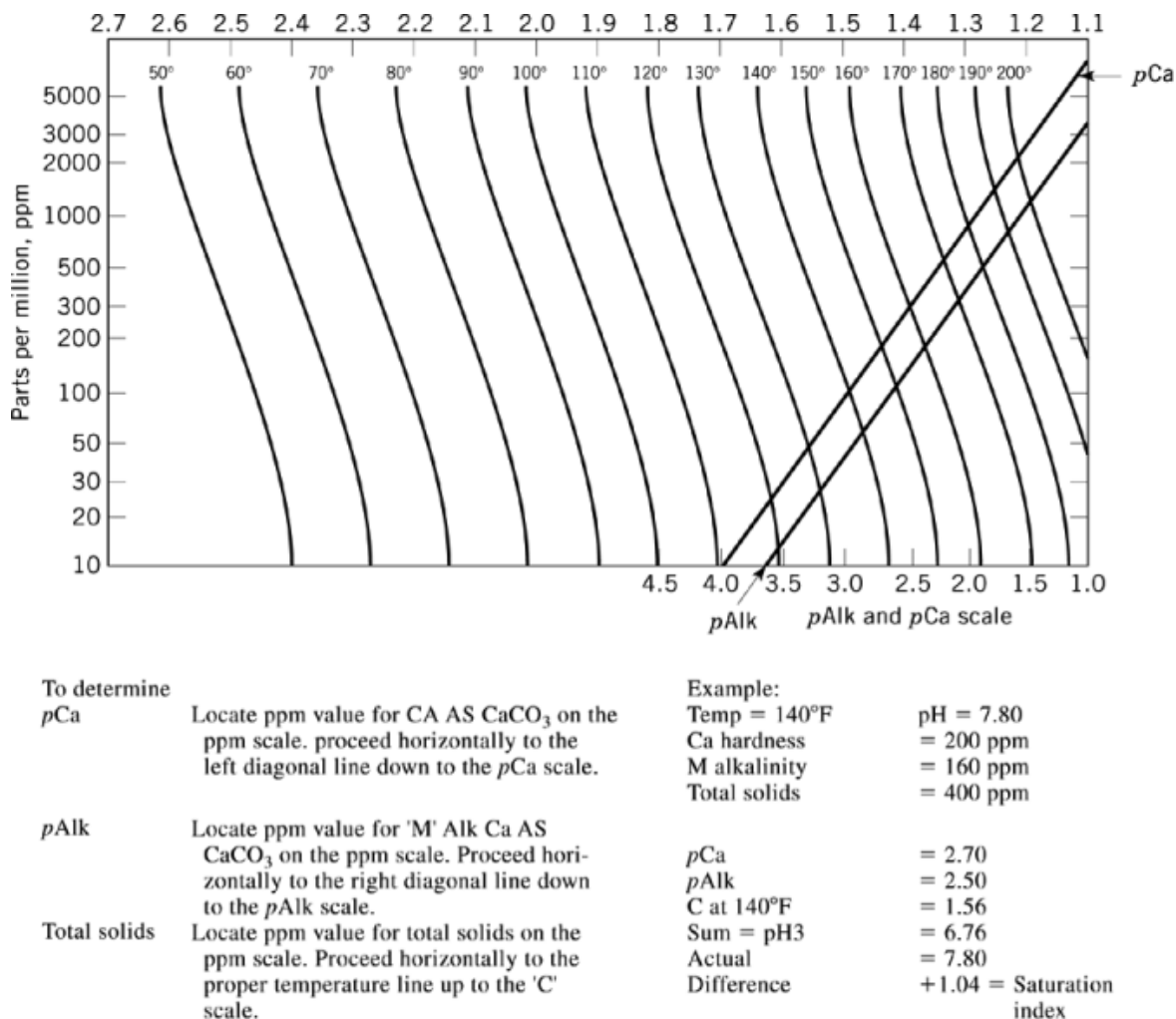
$$\text{Stability index} = 2(\text{pH}_s) - \text{pH}_a$$

Where waters have a stability index of 6.0 or less, scaling increases and the tendency to corrode decreases. Where the stability index exceeds 7.0, scaling may not occur at all. As the stability index rises above 7.5 or 8.0, the probability of corrosion increases. Use of the LSI together with the Stability Index contributes to more accurate prediction of the scaling or corrosive tendencies of a water.

A uniform coating of calcium carbonate deposited on the metal surfaces physically segregates the metal from the corrosive environment. To develop the positive LSI required to deposit calcium carbonate, it is usually necessary to adjust the pH or calcium content of the water. Soda ash, caustic soda, or lime (calcium hydroxide) may be used for this adjustment. Lime is usually the most economical alkali because it raises the calcium content as well as the alkalinity.

Theoretically, controlled deposition of calcium carbonate scale can provide a film thick enough to protect, yet thin enough to allow adequate heat transfer. However, low temperature areas do not permit the development of sufficient scale for corrosion protection, and excessive scale forms in high temperature areas and interferes with heat transfer. Therefore, this approach is not used for industrial cooling systems. Controlled calcium

## 24 WATER, INDUSTRIAL WATER TREATMENT

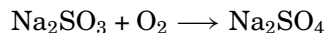


**Fig. 11.** A typical Langelier Saturation Index chart.

carbonate deposition has been used successfully in some waterworks distribution systems where substantial temperature increases are not encountered.

### 11.2. Mechanical and Chemical Deaeration

The corrosive qualities of water can be reduced by deaeration. Vacuum deaeration has been used successfully in once-through cooling systems. When all oxygen is not removed, catalyzed sodium sulfite can be used to remove the remaining oxygen. The sulfite reaction with dissolved oxygen is



The use of catalyzed sodium sulfite for chemical deaeration requires eight parts of catalyzed sodium sulfite for each part of dissolved oxygen. In certain systems where vacuum deaeration is already used, the application of



catalyzed sodium sulfite may be economically justified for removal of the remaining oxygen. The use of sodium sulfite may also be applicable to some closed loop cooling systems. In open recirculating cooling systems, continual replenishment of oxygen as the water passes over the cooling tower makes deaeration impractical.

### 11.3. Corrosion Inhibitors

A corrosion inhibitor is any substance that effectively decreases the corrosion rate when added to an environment. An inhibitor can be identified most accurately in relation to its function: removal of the corrosive substance, passivation, precipitation, or adsorption.

Deaeration (mechanical or chemical) removes the corrosive substance—oxygen.

Passivating (anodic) inhibitors form a protective oxide film on the metal surface; they are the best inhibitors because they can be used in economical concentrations and their protective films are tenacious and tend to be rapidly repaired if damaged.

Precipitating (cathodic) inhibitors are simply chemicals that form insoluble precipitates that can coat and protect the surface; precipitated films are not as tenacious as passive films and take longer to repair after a system upset.

Adsorption inhibitors have polar properties that cause them to be adsorbed on the surface of the metal; they are usually organic materials.

#### 11.3.1. Passivation Inhibitors

Examples of passivators (anodic inhibitors) include chromate, nitrite, molybdate, and orthophosphate. All are oxidizers and promote passivation by increasing the electrical potential of the iron. Chromate and nitrite do not require oxygen, and thus, can be the most effective. Chromate is an excellent aqueous corrosion inhibitor, particularly from a cost perspective. However, owing to health and environmental concerns, use of chromate has decreased significantly and will probably be outlawed soon. Nitrite is also an effective inhibitor, but in open systems it tends to be oxidized to nitrate.

Both molybdate and orthophosphate are excellent passivators in the presence of oxygen. Molybdate can be an effective inhibitor, especially when combined with other chemicals. Orthophosphate is not really an oxidizer *per se*, but becomes one in the presence of oxygen. If iron is put into a phosphate solution without oxygen present, the corrosion potential remains active and the corrosion rate is not reduced. However, if oxygen is present, the corrosion potential increases in the noble direction and the corrosion rate decreases significantly.

A negative attribute of orthophosphate is its tendency to precipitate with calcium hardness found in natural waters. In recent years, deposit control agents that prevent this deposition have been developed. Owing to its relatively low cost, orthophosphate is widely used as an industrial corrosion inhibitor.

#### 11.3.2. Precipitating Inhibitors

As discussed earlier, the localized pH at the cathode of the corrosion cell is elevated due to the generation of hydroxide ions. Precipitating inhibitors form complexes that are insoluble at this high pH (1–2 pH units above bulk water), but whose deposition can be controlled at the bulk water pH (typically 7–9 pH). A good example is zinc, which can precipitate as hydroxide, carbonate, or phosphate. Calcium carbonate and calcium orthophosphate are also precipitating inhibitors. Orthophosphate thus exhibits a dual mechanism, acting as both an anodic passivator and a cathodic precipitator.

#### 11.3.3. Copper Corrosion Inhibitors

The most effective corrosion inhibitors for copper and its alloys are the aromatic triazoles, such as benzotriazole (BZT) and tolyltriazole (TTA). These compounds bond directly with cuprous oxide ( $\text{Cu}_2\text{O}$ ) at the metal surface,

forming a “chemisorbed” film. The plane of the triazole lies parallel to the metal surface, thus each molecule covers a relatively large surface area. The exact mechanism of inhibition is unknown. Various studies indicate anodic inhibition, cathodic inhibition, or a combination of the two. Other studies indicate the formation of an insulating layer between the water surface and the metal surface. A recent study supports the idea of an electronic stabilization mechanism. The protective cuprous oxide layer is prevented from oxidizing to the nonprotective cupric oxide. This is an anodic mechanism. However, the triazole film exhibits some cathodic properties as well.

In addition to bonding with the metal surface, triazoles bond with copper ions in solution. Thus dissolved copper represents a “demand” for triazole, which must be satisfied before surface filming can occur. Although the surface demand for triazole filming is generally negligible, copper corrosion products can consume a considerable amount of treatment chemical. Excessive chlorination will deactivate the triazoles and significantly increase copper corrosion rates. Due to all of these factors, treatment with triazoles is a complex process.

#### **11.3.4. Adsorption Inhibitors**

Adsorption inhibitors must have polar properties to be adsorbed and block the surface against further adsorption. Typically, they are organic compounds containing nitrogen groups, such as amines, and organic compounds containing sulfur or hydroxyl groups. The size, orientation, shape, and electrical charge distribution of the molecules are all important factors. Often, these molecules are surfactants and have dual functionality. They contain a hydrophilic group, which adsorbs onto the metal surface, and an opposing hydrophobic group, which prevents further wetting of the metal.

Glycine derivatives and aliphatic sulfonates are examples of compounds that can function in this way. The use of these inhibitors in cooling systems is usually limited by their biodegradability and their toxicity toward fish. In addition, they can form thick, oily surface films, that may severely retard heat transfer.

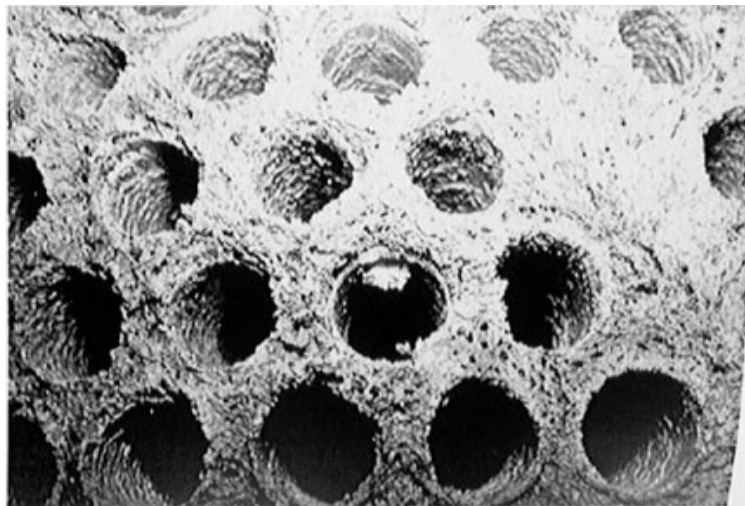
#### **11.3.5. Silicates**

For many years, silicates have been used to inhibit aqueous corrosion, particularly in potable water systems. Probably due to the complexity of silicate chemistry, their mechanism of inhibition has not yet been firmly established. They are nonoxidizing and require oxygen to inhibit corrosion, so they are not passivators in the classical sense. Yet they do not form visible precipitates on the metal surface. They appear to inhibit by an adsorption mechanism. It is thought that silica and iron corrosion products interact. However, recent work indicates that this interaction may not be necessary. Silicates are slow-acting inhibitors; in some cases, 2 or 3 weeks may be required to establish protection fully. It is believed that the polysilicate ions or colloidal silica are the active species and these are formed slowly from monosilicic acid, which is the predominant species in water at the pH levels maintained in cooling systems.

## **12. Cooling System Deposits**

Deposit accumulations in cooling water systems reduce the efficiency of heat transfer and the carrying capacity of the water distribution system. In addition, the deposits cause oxygen differential cells to form. These cells accelerate corrosion and lead to process equipment failure. Deposits range from thin, tightly adherent films to thick, gelatinous masses, depending on the depositing species and the mechanism responsible for deposition.

Deposit formation is influenced strongly by system parameters, such as water and skin temperatures, water velocity, residence time, and system metallurgy. The most severe deposition is encountered in process equipment operating with high surface temperatures and/or low water velocities. With the introduction of high efficiency film fill deposit accumulation in the cooling tower packing has become an area of concern. Deposits are broadly categorized as scale or foulants.



**Fig. 12.** Calcium carbonate scaling of a surface condenser due to poor pH control.

### 12.1. Scale

Scale deposits are formed by precipitation and crystal growth at a surface in contact with water. Precipitation occurs when solubilities are exceeded either in the bulk water or at the surface. The most common scale-forming salts that deposit on heat transfer surfaces are those that exhibit retrograde solubility with temperature.

Although they may be completely soluble in the lower temperature bulk water, these compounds (eg, calcium carbonate, calcium phosphate, and magnesium silicate) supersaturate in the higher temperature water adjacent to the heat-transfer surface and precipitate on the surface.

Scaling is not always related to temperature. Calcium carbonate and calcium sulfate scaling occur on unheated surfaces when their solubilities are exceeded in the bulk water. Metallic surfaces are ideal sites for crystal nucleation because of their rough surfaces and the low velocities adjacent to the surface. Corrosion cells on the metal surface produce areas of high pH, which promote the precipitation of many cooling water salts. Once formed, scale deposits initiate additional nucleation, and crystal growth proceeds at an accelerated rate.

Scale control can be achieved through operation of the cooling system at subsaturated conditions or through the use of chemical additives. The most direct method of inhibiting formation of scale deposits is operation at subsaturation conditions, where scale-forming salts are soluble. For some salts, it is sufficient to operate at low cycles of concentration and/or control pH. However, in most cases, high blowdown rates and low pH are required so that solubilities are not exceeded at the heat transfer surface. In addition, it is necessary to maintain precise control of pH and concentration cycles. Minor variations in water chemistry or heat load can result in scaling (Fig. 12).

#### 12.1.1. Threshold Inhibitors

Deposit control agents that inhibit precipitation at dosages far below the stoichiometric level required for sequestration or chelation are called *threshold inhibitors*. These materials affect the kinetics of the nucleation and crystal growth of scale-forming salts and permit supersaturation without scale formation. Threshold inhibitors function by an adsorption mechanism. As ion clusters in solution become oriented, metastable microcrystallites (highly oriented ion clusters) are formed. At the initial stage of precipitation, the microcrystallite can either continue to grow (forming a larger crystal with a well defined lattice) or dissolve. Threshold inhibitors prevent precipitation by adsorbing on the newly emerging crystal, blocking active growth sites. This inhibits further

growth and favors the dissolution reaction. The precipitate dissolves and releases the inhibitor, which is then free to repeat the process.

Threshold inhibitors delay or retard the rate of precipitation. Crystals eventually form, depending on the degree of supersaturation and system retention time. After stable crystals appear, their continued growth is retarded by adsorption of inhibitor. The inhibitor blocks much of the crystal surface, causing distortions in the crystal lattice as growth continues. The distortions (defects in the crystal lattice) create internal stresses, making the crystal fragile. Tightly adherent scale deposits do not form, because crystals that form on surfaces in contact with flowing water cannot withstand the mechanical force exerted by the water. The adsorbed inhibitor also disperses particles, by virtue of its electrostatic charge, and prevents the formation of strongly bound agglomerates.

The most commonly used scale inhibitors are low molecular weight acrylate polymers and organophosphorus compounds (phosphonates). Both classes of materials function as threshold inhibitors; however, the polymeric materials are more effective dispersants. Selection of a scale control agent depends on the precipitating species and its degree of supersaturation. The most effective scale control programs use both a precipitation inhibitor and a dispersant. In some cases this can be achieved with a single component (eg, polymers used to inhibit calcium phosphate at near neutral pH).

## 12.2. Fouling

Fouling occurs when insoluble particulates suspended in recirculating water form deposits on a surface. Fouling mechanisms are dominated by particle–particle interactions that lead to the formation of agglomerates. At low water velocities, particle settling occurs under the influence of gravity. Parameters that affect the rate of settling are particle size, relative liquid and particle densities, and liquid viscosity. The relationships of these variables are expressed by Stokes' law. The most important factor affecting the settling rate is the size of the particle. Because of this, the control of fouling by preventing agglomeration is one of the most fundamental aspects of deposition control.

Foulants enter a cooling system with makeup water, airborne contamination, process leaks, and corrosion. Most potential foulants enter with makeup water as particulate matter, such as clay, silt, and iron oxides. Insoluble aluminum and iron hydroxides enter a system from makeup water pretreatment operations. Some well waters contain high levels of soluble ferrous iron that is later oxidized to ferric iron by dissolved oxygen in the recirculating cooling water. Because it is insoluble, the ferric iron precipitates. The steel corrosion process is also a source of ferrous iron and, consequently, contributes to fouling.

Both iron and aluminum are particularly troublesome because of their ability to act as coagulants. Also, their soluble and insoluble hydroxide forms can each cause precipitation of some water treatment chemicals, such as orthophosphate. Airborne contaminants usually consist of clay and dirt particles but can include gases such as hydrogen sulfide, which forms insoluble precipitates with many metal ions. Process leaks introduce a variety of contaminants that accelerate deposition and corrosion.

Foulants, such as river water silt, enter the system as finely dispersed particles, which can be as small as 1–100 nm. The particles carry an electrostatic charge, which causes similarly charged particles to repel each other, favoring their dispersion. The net charge a particle carries depends on the composition of the water. Cycling of cooling water increases the concentration of counter-charged ions capable of being electrostatically attracted to and adsorbed onto a charged particle. As counterions adsorb, the net charge of the particle decreases. Particles begin to agglomerate and grow in size as their repulsive forces are diminished.

Settling occurs when the energy imparted by fluid velocity can no longer suspend the particle, due to agglomeration and growth. After particles have settled, the nature of the deposit depends on the strength of the attractive forces between the particles themselves (agglomerate strength) and between the particles and the surface they contact. If attractive forces between particles are strong and the particles are not highly

hydrated, deposits are dense and well structured; if the forces are weak, the deposits are soft and pliable. Deposition continues as long as the shear strength of the deposit exceeds the shear stress of the flowing water

### 12.3. Removal of Particulate Matter

The amount of particulate entering a cooling system with the makeup water can be reduced by filtration and/or sedimentation processes. Particulate removal can also be accomplished by filtration of recirculating cooling water. These methods do not remove all of the suspended matter from the cooling water. The level of fouling experienced is influenced by the effectiveness of the particular removal scheme employed, the water velocities in the process equipment, and the cycles of concentration maintained in the cooling tower.

### 12.4. High Water Velocities

The ability of high water velocities to minimize fouling depends on the nature of the foulant. Clay and silt deposits are more effectively removed by high water velocities than aluminum and iron deposits, which are more tacky and form interlocking networks with other precipitates. Operation at high water velocities is not always a viable solution to clay and silt deposition because of design limitations, economic considerations, and the potential for erosion corrosion.

### 12.5. Dispersants

Dispersants are materials that suspend particulate matter by adsorbing onto the surface of particles and imparting a high charge. Electrostatic repulsion between like-charged particles prevents agglomeration, which reduces particle growth. The presence of a dispersant at the surface of a particle also inhibits the bridging of particles by precipitates that form in the bulk water. The adsorption of the dispersant makes particles more hydrophilic and less likely to adhere to surfaces. Thus dispersants affect both particle-to-particle and particle-to-surface interactions.

The most effective and widely used dispersants are low molecular weight anionic polymers. Dispersion technology has advanced to the point at which polymers are designed for specific classes of foulants or for a broad spectrum of materials. Acrylate-based polymers are widely used as dispersants. They have advanced from simple homopolymers of acrylic acid to more advanced copolymers and terpolymers. The performance characteristics of the acrylate polymers are a function of their molecular weight and structure, along with the types of monomeric units incorporated into the polymer backbone.

### 12.6. Surfactants

Surface-active or wetting agents are used to prevent fouling by insoluble hydrocarbons. They function by emulsifying the hydrocarbon through the formation of microdroplets containing the surfactant. The hydrophobic (water hating) portion of the surfactant is dissolved within the oil drop, while the hydrophilic (water loving) portion is at the surface of the droplet. The electrostatic charge imparted by hydrophilic groups causes the droplets to repel each other, preventing coalescence. Through a similar process, surfactants also assist in the removal of hydrocarbon-containing deposits.

Cooling water systems, particularly open recirculating systems, provide a favorable environment for the growth of microorganisms. Microbial growth on wetted surfaces leads to the formation of biofilms. If uncontrolled, such films cause fouling, which can adversely affect equipment performance, promote metal corrosion, and accelerate wood deterioration. These problems can be controlled through proper biomonitoring and application of appropriate cooling water antimicrobials.

### 13. Biofouling

Microbiological fouling in cooling systems is the result of abundant growth of algae, fungi, and bacteria on surfaces. Once-through and open or closed recirculating water systems may support microbial growth, but fouling problems usually develop more quickly and are more extensive in open recirculating systems. Once-through cooling water streams generally contain relatively low levels of the nutrients essential for microbial growth, so growth is relatively slow. Open recirculating systems scrub microbes from the air and, through evaporation, concentrate nutrients present in makeup water. As a result, microbe growth is more rapid. Process leaks may contribute further to the nutrient load of the cooling water. Reuse of waste water for cooling adds nutrients and also contributes large amounts of microbes to the cooling system.

In addition to the availability of organic and inorganic nutrients, factors such as temperature, normal pH control range, and continuous aeration of the cooling water contribute to an environment that is ideal for microbial growth. Sunlight necessary for growth of algae may also be present. As a result, large, varied microbial populations may develop.

The outcome of uncontrolled microbial growth on surfaces is “slime” formation. Slimes typically are aggregates of biological and nonbiological materials. The biological component, known as the biofilm, consists of microbial cells and their by-products. The predominant by-product is extracellular polymeric substance (EPS), a mixture of hydrated polymers. These polymers form a gel-like network around the cells and appear to aid attachment to surfaces. The nonbiological components can be organic or inorganic debris from many sources that have become adsorbed to or embedded in the biofilm polymer.

Slimes can form throughout once-through and recirculating systems and may be seen or felt where accessible. In nonexposed areas, slimes can be manifested by decreased heat transfer efficiency or reduced water flow. Wood-destroying organisms may penetrate the timbers of the cooling tower, digesting the wood and causing collapse of the structure. Microbial activity under deposits or within slimes can accelerate corrosion rates and even perforate heat exchanger surfaces.

#### 13.1. Microorganisms

The microorganisms that form slime deposits in cooling water systems are common soil, aquatic, and airborne microbes. These microbes may enter the system with makeup water, either in low numbers from fresh water sources or in high numbers when the makeup is waste water. Significant amounts may also be scrubbed from the air as it is drawn through the cooling tower. Process leaks may contribute microorganisms as well.

##### 13.1.1. *Bacteria*

A wide variety of bacteria can colonize cooling systems. Spherical, rod-shaped, spiral, and filamentous forms are common. Some produce spores to survive adverse environmental conditions such as dry periods or high temperatures. Both aerobic bacteria (which thrive in oxygenated waters) and anaerobic bacteria (which are inhibited or killed by oxygen) can be found in cooling systems.

##### 13.1.2. *Fungi*

Two forms of fungi commonly encountered are molds (filamentous forms) and yeasts (unicellular forms). Molds can be quite troublesome, causing white rot or brown rot of the cooling tower wood, depending on whether they are cellulolytic (attack cellulose) or lignin degrading. Yeasts are also cellulolytic. They can produce slime in abundant amounts and preferentially colonize wood surfaces.

##### 13.1.3. *Algae*

Algae are photosynthetic organisms. Green and blue-green algae are common in cooling systems (blue-green algae are now classified with the bacteria and are called cyanobacteria). Various types of algae can be

responsible for green growths that block screens and distribution decks. Severe algae fouling can ultimately lead to unbalanced water flow and reduced cooling tower efficiency. Diatoms (algae enclosed by a siliceous cell wall) may also be present but generally do not play a significant role in cooling system problems.

#### 13.1.4. Biofilms

Microbiologists recognize two different populations of microorganisms. Free-floating (planktonic) populations are found in the bulk water. Attached (sessile) populations colonize surfaces. The same kinds of microorganisms can be found in either population, but the sessile population is responsible for biofouling.

When fouling occurs, even mechanical cleaning does not remove all traces of the biofilm. Previously fouled and cleaned surfaces are more rapidly colonized than new surfaces. Residual biofilm materials promote colonization and reduce the lag time before significant fouling reappears.

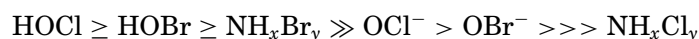
Biofilms on heat exchange surfaces act as insulating barriers. Heat exchanger performance begins to deteriorate as soon as biofilm thickness exceeds that of the laminar flow region. Microbes and hydrated biopolymers contain large amounts of water, and biofilms can be more than 90% water by weight. As a result, biofilms have thermal conductivities close to that of water, and in terms of heat transfer efficiency, a biofilm is the equivalent of a layer of stagnant water along the heat exchange surface.

Biofilms can promote corrosion of fouled metal surfaces in a variety of ways. This is referred to as microbially influenced corrosion. Microbes act as biological catalysts promoting conventional corrosion mechanisms: the simple, passive presence of the biological deposit prevents corrosion inhibitors from reaching and passivating the fouled surface; microbial reactions can accelerate ongoing corrosion reactions; and microbial by-products can be directly aggressive to the metal.

### 13.2. Oxidizing Antimicrobials

The oxidizing antimicrobials commonly used in industrial cooling systems are the halogens, chlorine and bromine, in liquid and gaseous form; organic halogen donors; chlorine dioxide; and to a limited extent, ozone. Oxidizing antimicrobials oxidize or accept electrons from other chemical compounds. Their mode of antimicrobial activity can be direct chemical degradation of cellular material or deactivation of critical enzyme systems within the bacterial cell. An important aspect of antimicrobial efficiency is the ability of the oxidizing agent to penetrate the cell wall and disrupt metabolic pathways.

The relative microbiological control ability of typical halogens is as follows:



Cooling water pH affects oxidizing antimicrobial efficacy. The pH determines the relative proportions of hypochlorous acid and hypochlorite ion or, in systems treated with bromine donors, hypobromous acid and hypobromite ion. The acid forms of the halogens are usually more effective antimicrobials than the dissociated forms. Under some conditions, hypochlorous acid is 80 times more effective in controlling bacteria than the hypochlorite ion. Hypochlorous acid predominates below a pH of 7.6. Hypobromous acid predominates below pH 8.7, making bromine donors more effective than chlorine donors in alkaline cooling waters, especially where contact time is limited.

Antimicrobial efficacy is also affected by demand in the cooling water system, specifically demand exerted by ammonia. Chlorine reacts with ammonia to form chloramines, which are not as efficacious as hypochlorous acid or the hypochlorite ion in microbiological control. Bromine reacts with ammonia to form bromamines. Unlike chloramines, bromamines are unstable and reform hypobromous acid.

Most microbes in cooling systems can be controlled by chlorine or bromine treatment if exposed to a sufficient residual for a long enough time. A free chlorine residual of 0.1–0.5 ppm is adequate to control bulk water organisms if the residual can be maintained for a sufficient period of time.

## 32 WATER, INDUSTRIAL WATER TREATMENT

Continuous chlorination of a cooling water system often seems most prudent for microbial slime control. However, it is economically difficult to maintain a continuous free residual in some systems, especially those with process leaks. In some high demand systems it is often impossible to achieve a free residual, and a combined residual must be accepted. In addition, high chlorine feed rates, with or without high residuals, can increase system metal corrosion and tower wood decay. Supplementing with nonoxidizing antimicrobials is preferable to high chlorination rates.

Sodium hypochlorite and calcium hypochlorite are chlorine derivatives formed by the reaction of chlorine with hydroxides. The application of hypochlorite to water systems produces the hypochlorite ion and hypochlorous acid, just as the application of chlorine gas does.

Halogen donors are chemicals that release active chlorine or bromine when dissolved in water. After release, the halogen reaction is similar to that of chlorine or bromide from other sources. Solid halogen donors commonly used in cooling water systems include 1-bromo-3-chloro-5,5-dimethylhydantoin, 1,3-dichloro-5,5-dimethylhydantoin, and sodium dichloroisocyanurate.

Chlorine dioxide,  $\text{ClO}_2$ , is another chlorine derivative. This unstable, potentially explosive gas must be generated at the point of application. The most common method of generating  $\text{ClO}_2$  is through the reaction of chlorine gas with a solution of sodium chlorite.

### 13.3. Ozone

Ozone is an allotropic form of oxygen,  $\text{O}_3$ . Because it is an unstable gas, it must be generated at the point of use. Ozone is an effective, clean oxidizing agent possessing powerful antibacterial and antiviral properties.

### 13.4. Nonoxidizing Antimicrobials

Nonoxidizing antimicrobials usually control growths by one of two mechanisms. In one, microbes are inhibited or killed as a result of damage to the cell membrane. In the other, microbial death results from damage to the biochemical machinery involved in energy production or energy utilization.

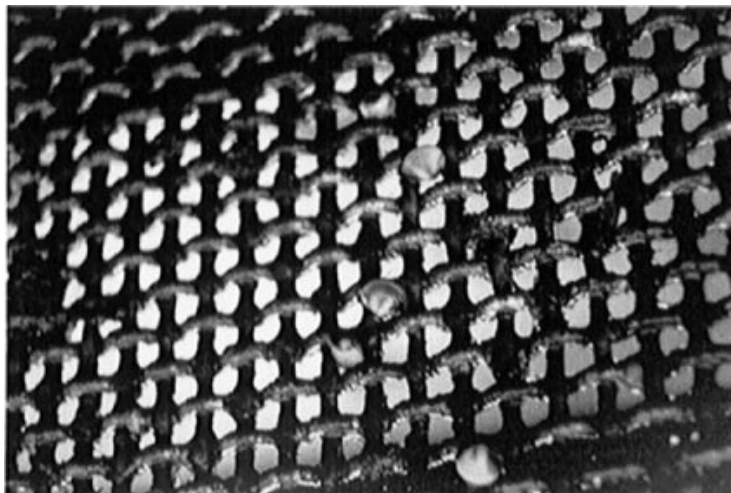
Quaternary ammonium compounds (quats) are cationic surface-active molecules. They damage the cell membranes of bacteria, fungi, and algae. As a result, compounds that are normally prevented from entering the cell are able to penetrate this permeability barrier. Conversely, nutrients and essential intracellular components concentrated within the cell leak out. Growth is hindered, and the cell dies. At low concentrations, quats are biostatic because many organisms can survive in a damaged state for some time. However, at medium to high concentrations, quats can control the organisms.

Many antimicrobials interfere with energy metabolism. Because all microbial activity ultimately depends on the orderly transfer of energy, it can be anticipated that interference with the many energy-yielding or energy-trapping reactions will have serious consequences for the cell. Antimicrobials known to inhibit energy metabolism include organotin, bis(trichloromethyl) sulfone, methylenebis-(thiocyanate) (MBT),  $\beta$ -bromo- $\beta$ -nitrostyrene (BNS), dodecylguanidine salts, and bromonitropropanediol (BNPD). All of these compounds are effective when applied in sufficient concentrations. Dodecylguanidine salts also have surfactant properties, which probably contribute to their effectiveness.

## 14. Macrofouling Organisms

Fouling caused by large organisms, such as oysters, mussels, clams, and barnacles, is referred to as macrofouling. Typically, organisms are a problem only in large once-through cooling systems or low cycle cooling systems that draw cooling water directly from natural water sources. Water that has been processed by an influent clarification and disinfection system is usually free of the larvae of macrofouling organisms.





**Fig. 13.** Juvenile Asiatic clams passing through a water intake screen.

Macrofouling has always been a concern in certain regions of the United States, especially in coastal areas. However, in the last 10 years, the incidence of problems in the United States caused by macrofouling has increased dramatically. This is due primarily to the “invasion” of two organisms that were accidentally introduced to this country: the Asiatic clam and the zebra mussel. Both organisms have flourished and represent a significant threat to system reliability. Adding to the problem is the decreased use of chlorine and heavy metal antimicrobials, which permits the infiltration and growth of macrofouling organisms in plant water systems.

## 15. Asiatic Clams

Asiatic clams are freshwater mollusks. They probably originated in China or eastern Asia and were introduced into North America and Europe in the past century. They were originally found in warm water but their territory now extends to Minnesota. They have not yet been seen in Canadian rivers or lakes.

Asiatic clams do not attach to surfaces but burrow into sediments in their natural environment. Larvae and juvenile clams easily pass through intake screens (Fig. 13) and settle in low flow areas. Within 6 months to 1 yr, the clams grow to 1.5–2.54 cm in size. When a clam dies, the shell gapes open. Shells of living or dead organisms are carried by water flow and can wedge in condenser or heat exchanger tubes. Once a shell is wedged in a tube, other shells and debris collect and plug the tube further (Fig. 14). The Asiatic clam reaches adulthood in about 1 yr and reproduces in warm months, releasing thousands of larvae into the system.

### 15.1. Thermal Treatment (Thermal Backwash)

The organisms that cause macrofouling can be killed by heated water. Some systems are designed to allow the heated water from the outlet of the condenser to be recirculated back to the intake. As the water recirculates, it is heated and improves macrofouling control. A 15- to 60-min exposure to water at 40°C or higher has effectively controlled zebra mussels. Thermal treatment is not used extensively because most systems are not designed to recirculate water. Also, when heated water is recirculated the system cooling capacity is greatly diminished.



**Fig. 14.** Surface condenser infested with adult Asiatic clams.

### 15.2. Oxidizing Antimicrobials

The application of an oxidizing antimicrobial such as chlorine for the control of undesirable organisms is a well-known and long-practiced procedure. Chlorine is toxic to all living organisms from bacteria to humans. However, in the case of hard-shelled creatures, including some mollusks and crustaceans, exposure is not easily accomplished. Some mollusks (eg, oysters, blue mussels, Asiatic clams, and zebra mussels) and crustaceans (eg, barnacles) have sensitive chemoreceptors that detect the presence of oxidizing chemicals such as chlorine (hypochlorite), bromine (hypobromite), ozone, and hydrogen peroxide. When oxidizers are detected at life-threatening levels, the animal withdraws into its shell and closes up tightly to exclude the hostile environment. Animals like oysters and mussels can remain closed for days to weeks if necessary. There is evidence to suggest that, during extended periods of continuous chlorination, the creatures may eventually die from asphyxiation rather than chlorine toxicity.

Even when their shells are closed, the animals continue to sense their environment, and as soon as the oxidant level decreases, they reopen and resume siphoning. Continuous chlorination often fails to eradicate these macrofouling creatures because of interruptions in the feed, which can occur for various reasons, such as chlorine tank changeover or plugging of feedlines. If the interruption lasts long enough (1 h or possibly less), the animals have time to reoxygenate their tissues between the extended periods of chlorination. Any oxidant, such as chlorine, bromine, or ozone, elicits the same response from these creatures. Therefore, only continuous, uninterrupted applications are successful.

### 15.3. Nonoxidizing Antimicrobials

There are several categories of nonoxidizing antimicrobials that have proven to be effective in controlling macrofouling organisms. Quaternary amine compounds and certain surfactants have been applied to infested systems for relatively short intervals (6–48 h). These compounds do not trigger the chemoreceptors of the mollusks. The mollusks continue to filter feed and ingest a lethal dosage of the antimicrobial throughout the exposure period. These compounds produce a latent mortality effect; the mollusks may not die until several hours after the antimicrobial application. Cold water temperatures may extend this latent mortality effect and may also require slightly higher feed rates and longer feed durations due to slower organism metabolism.

The advantages of a nonoxidizing antimicrobial program include ease of handling, short application time, and relatively low toxicity to other aquatic organisms. In addition, some of these compounds can be readily detoxified.

## BIBLIOGRAPHY

“Water (Industrial)” in *ECT* 1st ed., Vol. 14, pp. 926–946, by E. P. Partridge, Hall Laboratories, Inc.; “Water, Industrial Water Treatment” in *ECT* 2nd ed., Vol. 22, pp. 65–82, by J. K. Rice and D. E. Simon II, Cyrus Wm. Rice Division, NUS Corporation, “Water (Industrial Treatment)” in *ECT* 3rd ed., Vol. 24, pp. by S. Sussman, Olin Water Services.

### General References

1. J. F. Malina and F. G. Pohland, *Design of Anaerobic Processes for the Treatment of Industrial and Municipal Wastes*, Technomic Publishing, Lancaster, Pa., 1992.
2. C. E. Hamilton, ed., *Manual on Water*, ASTM Special Publication 442A, American Society for Testing and Materials, Philadelphia, Pa., 1978, 472 pp.
3. *Standard Methods for the Examination of Water and Wastewater*, 15th ed., American Public Health Association, Washington, D.C.
4. F. van der Leeden and co-workers, *The Water Encyclopedia*, Lewis Publishers, Chelsea, Mich., 1990.
5. *The Nalco Water Handbook*, McGraw-Hill, Inc. Publishers, New York, NY, 1979.
6. *Betz Handbook of Industrial Water Conditioning*, Ninth Edition, Trevese, PA, 1991.
7. *The ASME Handbook on Water Technology for Thermal Power Systems*, The American Society of Mechanical Engineers, New York, NY, 1989.
8. *Metals Handbook*, Ninth Edition, Volume 13, ASM International, Metals Park, Ohio, 1987.
9. *CRTD* 35, (1995).
10. *Consensus on Operating Practices for The Control of Feedwater and Boiler Water Chemistry in Modern Industrial Boilers*, The American Society of Mechanical Engineers, New York, NY, 1994.

JAMES ROBINSON  
Betz Dearborn

### Related Articles

Water, municipal water treatment; Reverse osmosis; Corrosion and corrosion control; Water, pollution; Filtration