

CHAPTER 1

INTRODUCTION

The Cooling System

An understanding of the relationship between cooling water and the build up of deposits and corrosion of heat transfer surfaces requires an awareness of cooling system characteristics. There are basically three types of cooling systems: once-through, closed recirculating, and open recirculating systems (Fig.1.1).

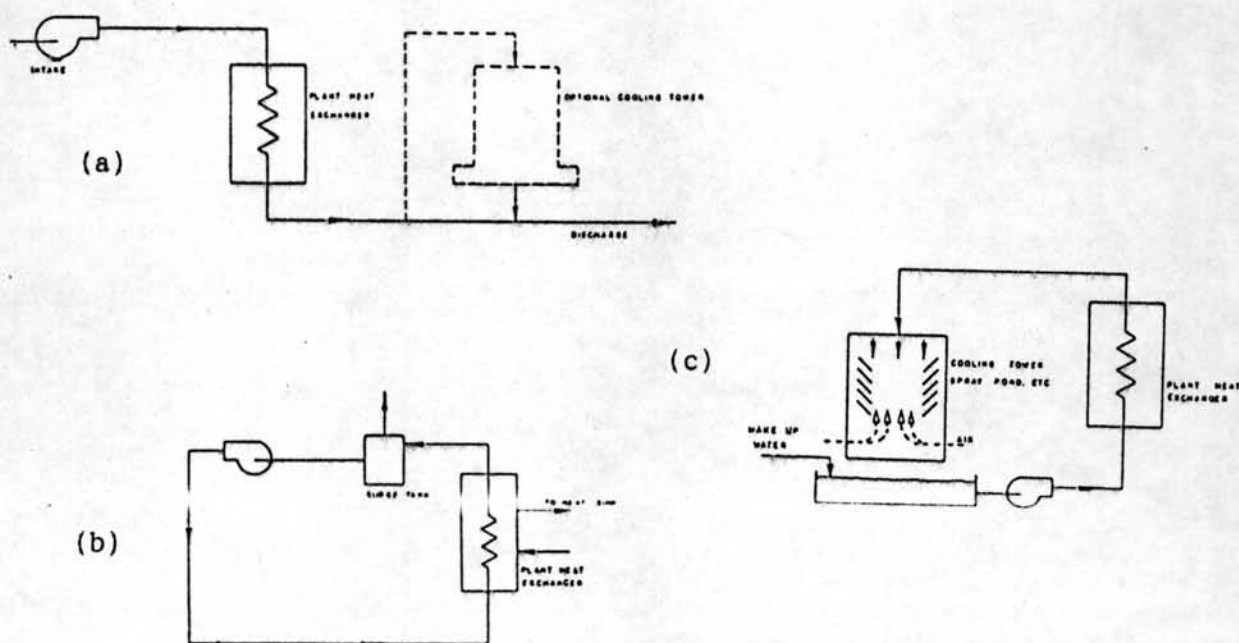


Fig. 1.1 Schematics of three types of cooling systems.

(a) Once-through system. (b) Closed recirculating system.

(c) Open recirculating system.

In once-through systems, the cooling water passes through the heat transfer equipment only once before it is discharged. Large volumes of water are used with only a small temperature increase across the exchanger. The mineral content of the water remains essentially the same. Water is usually drawn from such sources as rivers, lakes, and wells.

Closed recirculating systems have little water loss and continuously recirculate the same water. The heat absorbed from the heat transfer equipment is dissipated to another heat sink, which is cooled by other methods. Because there are no evaporative losses, the makeup water is minimal, and the mineral content remains essentially constant. However, corrosion by-products can easily accumulate and foul heat transfer equipment because there are no methods of removing them from the system. Operating temperatures of the closed recirculating systems range from cold (as in chilled-water systems) to hot (for engine cooling jackets).

Open recirculating systems continuously reuse the water that passes through the heat transfer equipment. Circulated water can be drawn from spray ponds or cooling tower basins. Evaporative cooling to the atmosphere dispels the unwanted heat transferred to the cooling water. The water then returns to the source and recirculates. In cooling tower operations, the water cascades over and down the tower, where evaporative heat transfer takes place. Make-up water is added to replace

the evaporative losses. Additional makeup water replaces the intentionally discharged water (blowdown) to maintain an acceptable level of dissolved minerals and suspended solids in the cooling water.

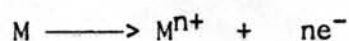
Open recirculating cooling systems are oxygen saturated and may contain a high level of dissolved solids. Inlet temperatures to the heat transfer equipment are usually higher than those for once-through cooling systems. Also there may be a larger temperature differential across the exchanger. These factors can significantly affect the buildup of deposits and deterioration of the heat transfer equipment. The problem of open recirculating system consists of corrosion problems, scale deposition and fouling deposition.

Corrosion Processes in Water-Recirculating Systems

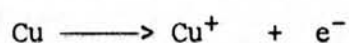
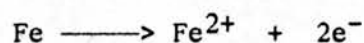
The corrosion processes and the fouling of heat transfer equipment must be understood if long-term reliability is to be achieved. Corrosion can be defined in a very practical sense as the deterioration of metal caused by the reaction with its surrounding environment. Because water is one of the most common heat transfer fluids, it is not surprising that most of the problems associated with corrosion and deposits are water related. However, dissolved gases (such as oxygen, carbondioxide, CO_2 , ammonia, and chlorine), dissolved salts (such as calcium, magnesium, chloride, sulfate, and

bicarbonate), and suspended solids make water something other than pure H_2O .

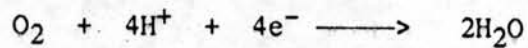
For the corrosion reactions to take place between water and the metal surface, a potential difference must exist between different areas on the surface. This causes the passage of electrical current through the metal from the area of high potential to low potential. Thus, corrosion of metals in contact with water is electrochemical in nature. The basic reactions occur at the region of lower potential, which is the anode. The dissolution reaction causes metal ions to form and go into solution. The anodic oxidation reaction can be generally represented by:



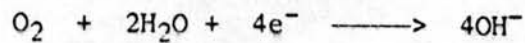
where M represents the metal that has been oxidized to its ionic form having a valence of n^{+} and the release of n electrons. For the more common heat transfer materials, the individual reactions are:



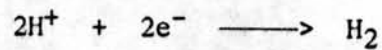
The liberated electrons that migrate through the metal to areas of higher potential are used in the reduction of other ions or oxygen in the water. These reductions occur at the cathodic site on the metal surface:



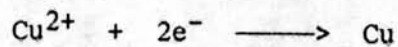
(Reduction of oxygen in acid solution)



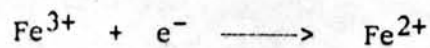
(Reduction of oxygen in neutral or alkaline solution)



(Hydrogen evolution)



(Metal deposition)

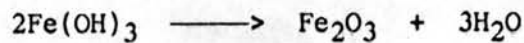
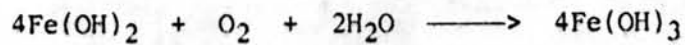


(reduction of metal ions)

Interaction between the products of the anodic and cathodic reactions can occur, forming solid corrosion products on the metal surface. For example, ferrous ions (Fe^{2+}) coming from the corrosion of metallic iron will react with the hydroxyl ions (OH^-) produced from the reduction of dissolved oxygen:



Ferrous hydroxide ($\text{Fe}(\text{OH})_2$) is further oxidized to form ferric hydroxide ($\text{Fe}(\text{OH})_3$), which is unstable and subsequently transformed to hydrated ferric oxide ($\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$) common red rust:



A buildup of rust occurs at the anodic sites, forming mounds known as tubercles. Under these mounds, localized corrosion continues to accelerate (Fig. 1.2) [1].

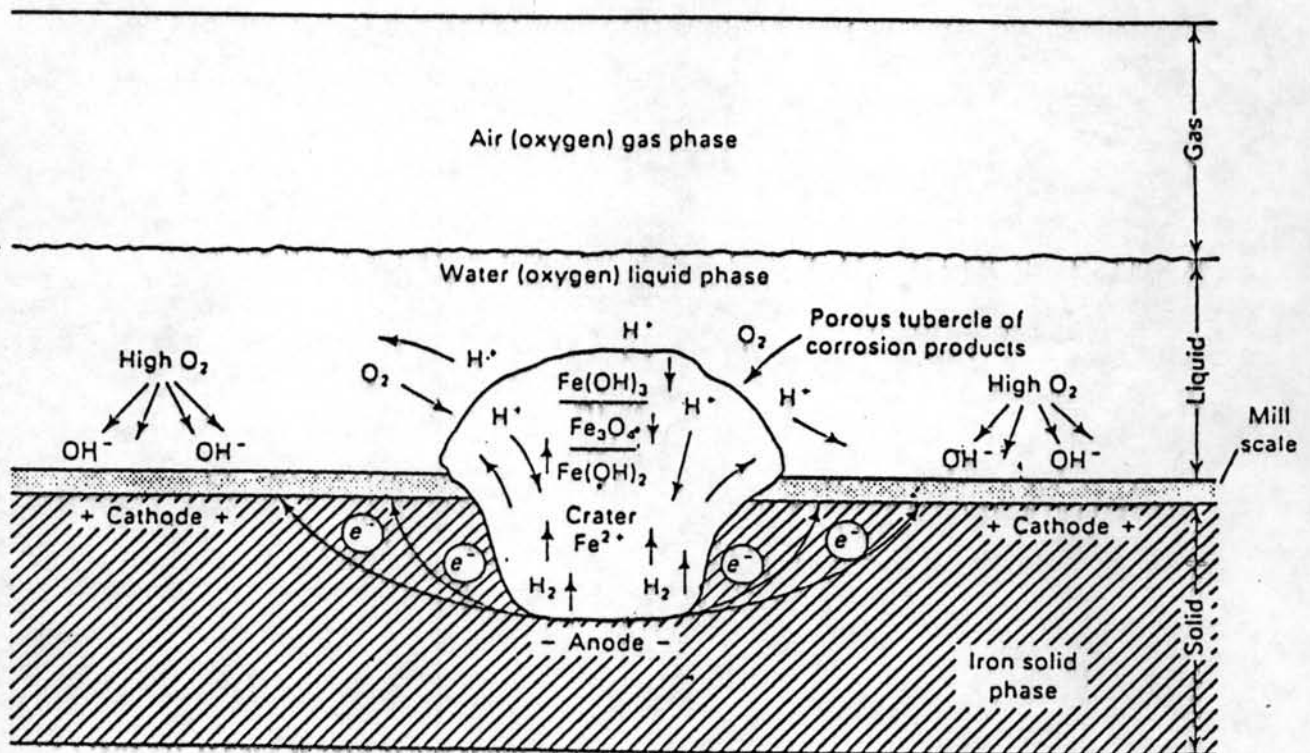
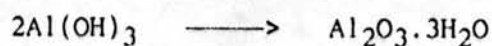
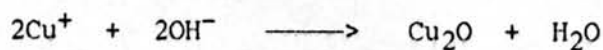


Fig. 1.2 Schematic of localized corrosion under a rust tubercle [1].

Not all corrosion products are detrimental. The protective oxide films on copper (cuprous oxide, Cu_2O) and aluminium (aluminium oxide, Al_2O_3) are the result of corrosion:



These films are self-limiting, inhibiting the corrosion process once they are fully developed.

The corrosion process between water and metal surfaces can take many forms [2]. The more common forms that have been observed in heat transfer equipment have the characteristics discussed in the following sections (additional information is available in the section "Forms of Corrosion" in this volume).

General corrosion, or uniform attack, occurs when the anodic areas on the metal surface keep shifting to different sites. This continual shifting results in relatively uniform metal removal. Because this type of corrosion can often be predicted, material loss can be taken into account.

Galvanic corrosion occurs when dissimilar materials are in contact in a conducting fluid (water). Accelerated corrosion

occurs with the least resistant alloy, while the more resistant alloy is protected. The resistance of alloys can generally be described by the galvanic series, which ranks materials according to their chemical reactivity in seawater. The metals closer to the active end of the series will behave as the anode and will corrode, but those closer to the noble end will behave as the cathode and will be protected. Table 1.1 lists an abridged galvanic series. The intensity of attack is related to the relative surface areas of the metals in electrical contact.

Large cathodic areas coupled to small anodic areas will aggravate galvanic corrosion and cause severe dissolution of the more active metal. The reverse situation—large anodic areas coupled to small cathodic areas—produces very little galvanic current.

Galvanic corrosion obviously must be considered in the design of heat transfer equipment. Alloys close to one another in the galvanic series should be used. Less obvious are the damaging effects that can occur when a dissolved noble metal is transported through the water and is capable of depositing on an active metal. For example, copper ions can plate out onto steel heat transfer tube surfaces, setting up local corrosion cells.

Erosion-corrosion is normally restricted to copper-base

Table 1.1 Galvanic series of some commercial metals and alloys
in seawater

Noble or cathodic
Platinum
Gold
Graphite
Titanium
Silver
Chlorimet 3 (62Ni-18Cr-18Mo)
Hastelloy C (62Ni-17Cr-15Mo)
18-8Mo stainless steel (passive)
18-8 stainless steel (passive) ;
Chromium stainless steel 11-30% Cr (passive)
Inconel (passive) (80Ni-13Cr-7Fe)
Nickel (passive)
Silver solder
Monel (70Ni-30Cu)
Cupronickels (60-90Cu, 40-10Ni)
Bronzes (Cu-Sn)
Copper
Brasses (Cu-Zn)
Chlorimet 2 (66Ni-32Mo-1Fe)
Hastelloy B (60Ni-30Mo-6Fe-1Mn)
Inconel (active)
Nickel (active)
Tin
Lead
Lead-tin solders
18-8Mo stainless steel (active)
18-8 stainless steel (active)
Ni-Resist (high-nickel cast iron)
Chromium stainless steel, 13% Cr (Active)
Cast iron
Steel or iron
Aluminium alloy 2024
cadmium
Aluminium alloy 1100
Zinc
Magnesium and magnesium alloys
Active or

source: Ref[2]

alloys. It occurs in areas where turbulence intensity at the metal surface is high enough to cause mechanical or electrochemical disruption of the protective film. Corrosion occurs at these sites and forms horseshoe-crescent-shaped indentations facing upstream of the water flow. The process is usually accelerated when abrasive solid particles, such as sand, are entrained in the water. Because turbulence increases with velocity, areas having higher water velocities are prone to attack. For example, turbulence intensity is much higher at tube inlets than it is several feet down the tube resulting in the phenomenon of inlet-end erosion corrosion.

Crevice corrosion is an electrochemical attack that is due to differences in the corrosive environment between a shielded area and its surroundings. Attack usually occurs in areas having a small volume of stagnant solution, such as at tube sheet supports, under deposits or tubercles, and at threaded joints. Corrosion is usually initiated because the oxygen concentration within the crevice is lower than that of the surrounding area. The outside area is higher in oxygen concentration and becomes the predominant cathodic region. Anodic dissolution occurs at the stagnant area. Once attack is underway, the area in the crevice or under a deposit becomes increasingly more aggressive because of pH depression and an increase in electrolyte concentration.

Pitting corrosion is one of the most insidious forms of

attack. It takes place at small discrete areas where overall metal loss is negligible. The pit develops at a localized anodic site on the surface and continues to grow because of a large cathodic area surrounding the anode. High concentrations of metal chlorides often develop within the pit and hydrolyze to produce an acidic pH environment. This solution remains stagnant, having a high salt content and low oxygen concentration. The reactions within the pit become self-sustaining (autocatalytic) with very little tendency for them to be suppressed, ultimately causing penetration through the base metal. Pitting corrosion has also been associated with both crevice and galvanic corrosion. Metal deposition (copper ions plated on a steel surface) can also create sites for pitting attack.

Influence of Water Quality

The corrosivity of water is significantly influenced by concentrations of dissolved species, including gasses, pH, temperature, suspended matter, and bacteria. The effects of these entities on corrosion are assumed to be independent; although this is not totally correct-interactions do exist-it is easier to visualize their contribution when they are considered separately.

Dissolved Gases

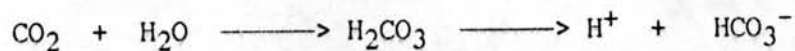
Dissolved oxygen is a major factor contributing to the natural corrosion of steel. It has been shown that oxygen is part of the overall electrochemical reactions occurring at the interface between the aqueous phase and the metal surface. Therefore, it is not surprising that steel corrosion is proportional to the oxygen content in the water. Oxygen solubility in water will vary with temperature, pressure, and electrolyte concentration. Increasing the temperature decreases oxygen solubility, but increasing the partial pressure of oxygen increases its solubility. Concentrated electrolytes decrease oxygen solubility (molar salt concentrations exist in pit cavities and crevices). For open recirculating cooling water systems, the concentration of dissolved oxygen is approximately 6 mg/l. The presence of oxygen is necessary for the formation of protective oxides on copper (Cu_2O), aluminium (Al_2O_3) and steel ($\delta\text{-Fe}_2\text{O}_3$). In the absence of dissolved oxygen, the corrosion of steel is greatly reduced. A uniform protective film of magnetite (Fe_3O_4) is formed according to the following reaction:



Overall, oxygen can have either a negative or a positive impact on the corrosion of steel. In aerated system, uneven distribution of corrosion products can form on the metal surface, giving rise to localized corrosion. Under deaerated conditions, the Fe_3O_4

film isolates the base metal from the water, drastically reducing corrosion.

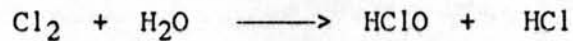
Carbon dioxide is more soluble than oxygen in pure water (1.3 g/l at 30°C, or 85°F) and will convert to carbonic acid (H_2CO_3), producing a solution having a pH of less than 6 where acid attack can predominate:



Adjusting the pH of the water upward redistributes the ratio of dissolved carbonic species. Carbonic acid will dissociate to form bicarbonate ions (HCO_3^-) and subsequently carbonate ions (CO_3^{2-}). The ratio of the various components can be calculated from the pH of the system. In open recirculating cooling water systems, the pH is usually controlled within the 7 to 8.5 range. Within this range, only the $\text{CO}_2/\text{HCO}_3^-$ ratio is important (The CO_3^{2-} concentration is negligible). Calcium ions (Ca^{2+}) in water will react with bicarbonate species to produce calcium carbonate (CaCO_3). This salt has a low solubility and will precipitate onto heat transfer surfaces (see the section "Calcium Carbonate"). The effect of CO_2 is most important in boiler condensate systems. Here, H_2CO_3 reacts with the steel to form ferrous bicarbonate ($\text{Fe}(\text{HCO}_3)_2$), which is a highly soluble salt. Rapid general thinning of steel can occur the addition of soluble amine inhibitors neutralizes the H_2CO_3 to suppress the corrosive attack. Copper alloys are also susceptible

to increased attack in the presence of CO_2 .

Chlorine is not a natural constituent of cooling waters, but is added for biological control. When dissolved in water, chlorine will convert to hypochlorous acid (HClO) and hydrochloric acid (HCl), which will suppress the pH:



Acid attack on steel is a concern when the pH falls below 7. Above this pH, the deleterious effects of chlorine are reduced. Adequate biological control can be achieved if the pH is maintained at approximately 7.5. However, chlorine will accelerate the corrosion of copper alloys, even at alkaline pHs. It is one of the most aggressive species to copper alloys in cooling waters: it can induce localized attack and degrade the protective Cu_2O film.

Ammonia. Another gas that can affect heat transfer equipment is ammonia (NH_3). Although its effect on ferrous alloys is minimal, it has a drastic impact on copper-rich brasses and alloys. These alloys can experience both rapid general thinning and stress-corrosion cracking (SCC). Ammonia is originally formed from the thermal degradation of various nitrogen-containing compounds added to a boiler to reduce ferrous corrosion. It forms a soluble complex with copper that can autocatalytically deteriorate the alloy in a short period of time.

Temperature

As previously stated, corrosion is an electrochemical phenomenon. It is not surprising that an increase in temperature will cause an increase in corrosion rates. Temperature plays a dual role with respect to oxygen corrosion. Increasing the temperature will reduce oxygen solubility. In open systems, in which oxygen can be released from the system, corrosion will increase up to a maximum at 80° C (175° F) where the oxygen solubility is 3 mg/l. Beyond this temperature, the reduced oxygen content limits the oxygen reduction, preventing occurrence of the iron dissolution process. Thus, the corrosion rate of carbon steel decreases, and at boiling water conditions, the temperature effect is similar to room temperature with a high oxygen content. For closed systems, in which oxygen cannot escape, corrosion continues to increase linearly with temperature. The other physicochemical properties affected by temperature are the diffusion of oxygen to the metal surface, the viscosity of water, and solution conductivity. Increasing the temperature will increase the rate of oxygen diffusion to the metal surface, thus increasing corrosion rate because more oxygen is available for the cathodic reduction process. The viscosity will decrease with increasing temperature, which will aid oxygen diffusion. Ionic mobility will also increase with temperature, increasing the overall conductivity of water.

An unusual temperature effect can occur with copper

alloys [3]. Temperature differences of at least 65°C (115°F) between the ends of copper conduits will cause the cold end to be cathodic to the hot end. Copper ions will migrate to the cold end and dissolve (corrode) at the hot end. At the cathode, copper ions will plate out, but at the anode, the surface will become rough and will pit. This effect is known as thermogalvanic attack.

One other effect of temperature should be noted, although it is not related to corrosion. An increase in temperature will decrease the solubility of many sparingly soluble inorganic salts. The solubility of CaCO_3 and calcium sulfate (CaSO_4) will decrease with an increase in temperature, precipitating and forming a thick barrier deposit at the hottest areas.

Suspended solids

Suspended matter, such as clays, silt, and corrosion products, is always present in open recirculating cooling water systems. Particulates scrubbed from the air add to the suspended solids loading. These materials are usually soft and nonabrasive. They are capable of depositing in low-flow areas, forming a physical barrier, and preventing oxygen from reaching the metal/solution interface. This buildup will contribute to the formation of differential aeration cells (crevice corrosion) and will promote localized attack.

Effect of pH

The normal pH range for an open recirculating cooling water system is 6.5 to 9. Closed systems operate at a pH of 8.5 to 9; in boilers, the pH of the water is often 11. These pH values are the bulk pH of the water, but the actual pH at the metal surface can be different, depending on prevailing surface reactions. Oxygen reduction will produce OH^- ions, raising the pH, but underdeposit corrosion products can depress the pH.

When the bulk water pH is moderately acidic (pH 5), uniform corrosion is the predominant form of attack, which increases with decreasing pH. In mineral acid (pH 4 or below), the protective oxide film dissolves, exposing bare metal surfaces. Corrosion is further accelerated when dissolved oxygen is reduced at the metal surface at low pH. Both hydrogen evolution and oxygen reduction become the prevalent cathodic reactions. As the pH increases above 4, iron oxides precipitate from solution to form deposits. uniform corrosion gradually decreases, but underdeposit attack begins because of the formation of Fe_2O_3 adhering to the surface. These deposits impede the diffusion of oxygen to the metal surface. As the pH increases, the nature of the iron oxide deposits changes from loosely adherent at pH 6 to hard and tenacious at pHs above 8. Although the corrosion of steel in aerated waters decreases within the normal operating pH range of 6.5 to 9, the rates are sufficiently high that chemical treatments must be added to these systems to bring the

rates within a manageable level of less than 0.13 mm/yr (5 mil/yr).

Copper alloys are not as sensitive to pH as carbon steel is. Acid pHs will accelerate general corrosion. As the pH increases, uniform corrosion decrease significantly. However, general thinning is not as severe a problem as the formation of cupric ions (Cu^{2+}), which can cathodically deposit on steel and create active sites for pitting attack.

Aside from the effect of pH on corrosion, increasing the pH of waters having moderate levels of calcium and alkaline values can result in the precipitation of CaCO_3 . The deposition of this alkaline scale can impede the diffusion of oxygen to metal surface in addition to forming a heat transfer barrier.

Dissolved Salts

Dissolved constituents in water can have a variety of effects, both individually and through their interactions. The effects include increased corrosion in addition to scale and deposit formation. Increasing the dissolved solids content of the water increases its conductivity. Galvanic effects due to the coupling of dissimilar metals are extended in water having a higher salt content compared to water of low conductivity.

Hardness ions (calcium and magnesium) and HCO_3^- ions are inhibitive and will suppress corrosion, but chloride (Cl^-) and

sulfate (SO_4^{2-}) ions are antagonistic and will increase the rate of some forms of corrosion. The aggressiveness of water can be reduced by increasing the concentration of hardness ions. Most water used for cooling have pH in the vicinity of neutral or above. This environment is very conducive to the formation of a protective film of CaCO_3 even when the water is below the saturation level for this salt. The actual mechanism that occurs at the water/metal surface interface is more involved than simple deposition of deposit. It is quite probable that CaCO_3 formation is due to electrochemical changes at the metal surface. The pH at the surface is usually higher than that of bulk water because of an increase in OH^- ion concentration, a reaction product of oxygen reduction.

The overall aggressiveness of water is related to its hardness and alkalinity. Soft waters which are low in calcium, are more corrosive than hard waters. Laboratory studies using three different waters of various compositions have shown that increased calcium concentration reduces general corrosion [4], as illustrated in Fig. 1.3.

The HCO_3^- ion is the predominate alkaline species in natural waters within the 6.5 to 9 pH range. Alone, it is a mild inhibitive species. Its reaction with Ca^{2+} ions is quite obvious, producing bulk precipitation of CaCO_3 once saturation is reached. Localized corrosion cells normally develop under the deposits. Increasing the bicarbonate concentration beyond that required for CaCO_3 saturation can be aggressive to steel

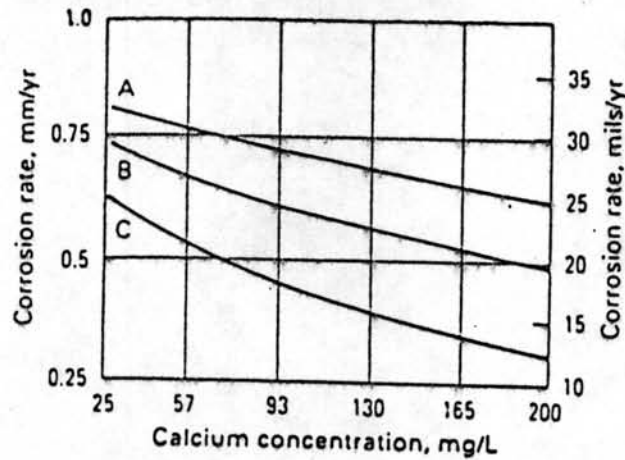


Fig. 1.3 Corrosion rate versus calcium concentration in three different waters. A, $\text{HCO}_3^- = 38 \text{ mg/l}$, $\text{Cl}^- = 78 \text{ mg/l}$, $\text{SO}_4^{2-} = 78 \text{ mg/l}$; B, $\text{HCO}_3^- = 100 \text{ mg/l}$, $\text{Cl}^- = 224 \text{ mg/l}$, $\text{SO}_4^{2-} = 224 \text{ mg/l}$; C, $\text{HCO}_3^- = 266 \text{ mg/l}$, $\text{Cl}^- = 644 \text{ mg/l}$, $\text{SO}_4^{2-} = 644 \text{ mg/l}$

due to the formation of nonprotective iron carbonate (FeCO_3) film.

Copper alloys are also attacked by high HCO_3^- concentrations. Greenish-blue nodules that consists of basic copper salts usually form at active pit sites.

Chlorine and SO_4^{2-} ions are known to have a deleterious effect on steel. Much of the antagonistic nature of Cl^- ions is due to their ability to adsorb on the metal surface and interfere with the formation of passive films. Pitting is the most common form of attack. The small exposed area where Cl^- ions have adsorbed are anodic to the large cathodic passive oxide surface. High current densities are generated at the Cl^-

site. Once corrosion begins, hydrolysis of the metal ions from the anodic reaction causes a decrease in pH, which discourages film repair and accelerates attack. The level of Cl^- ions needed to initiate attack can be as low as a few milligrams per litre for some stainless steels in high-purity waters. The more susceptible an alloy is to general attack, the less effect there is from Cl^- ions. Carbon steel will corrode in chloride-containing water primarily from uniform corrosion rather than localized attack.

Copper alloys are subject to degradation by Cl^- ions that modify the Cu_2O structure. The small, negatively charged Cl^- ion can migrate through the Cu_2O film to areas of high positive charge density (Cu_2O is a *p*-type semiconductor). Substitution of a monovalent charged chloride species for a divalent charged oxygen species can occur. To maintain electroneutrality, cuprous ions (Cu^+) are ejected (dissolved) into the aqueous phase. The loss of Cu^+ ions is, by definition, corrosion.

Sulfate ions are somewhat more elusive in their effect on corrosion. These ions do not appear to have the film-piercing properties of Cl^- ions. In fact, there is evidence that SO_4^{2-} ions may inhibit corrosion of some stainless steels [5].

Other ions found in cooling waters that have an effect on corrosion are manganese, sulfide (S^{2-}), phosphate (PO_4^{3-}), and nitrate (NO_3^-). Sodium (Na^+) and potassium (K^+) ions are considered

neutral species and have no discernible effect. Manganese is found in both well and surface waters and can cathodically deposit on stainless steels and copper-base alloys. Attack usually occur under these deposits. Sulfide ions from putrefaction of organic matter, sulfate-reducing bacteria, or pollution will attack copper-base alloys and steels.

The Cu_2O film becomes nonprotective through a substitution of S^{2-} ions for the oxygen ion, accelerating corrosion. Attack occurs on steel through the formation of ferrous sulfide (FeS). Deep pits will develop in both alloys.

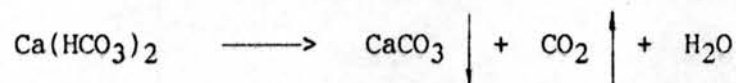
Phosphate ions can act as accelerator or as an inhibitor for steel corrosion, depending on its concentration. At low concentrations, PO_4^{3-} ions will cause pits to develop on the surface of the metal. Higher concentrations of 15 to 20 mg/l reverse this role, and the ion contributes to the stabilization of $\gamma\text{-Fe}_2\text{O}_3$. Nitrate ions can be reduced on steel surfaces, producing nitrites, NH_3 , and OH^- ions. Nitrite ions (NO_2^-) are inhibitory to copper and steel alloys, but NH_3 will attack copper.

Scale Deposition

Water-formed deposits, commonly referred to as scale, can be defined as a crystalline growth of an adherent layer (barrier) of insoluble salt or oxide on a heat exchanger surface.

The rate of formation is a complicated function of many variables, including temperature, concentration of scale-forming species, pH, water quality and hydrodynamic conditions. The normal solubilities of scales increase with temperature, but few for example, CaCO_3 and CaSO_4 , have the reverse trend. Unfortunately, these scales are commonly found in cooling water systems.

calcium carbonate is perhaps the most commonly found scale in cooling water systems. Calcium and bicarbonate alkalinity are both needed to form this extremely tenacious scale (alkalinity is the concentration of HCO_3^- , CO_3^{2-} , and OH^- ions present in the water). An increase in heat and/or pH will cause the HCO_3^- ions to decompose to CO_2 and CaCO_3 :



The greatest concentration of CaCO_3 will occur at the hottest areas along the heat transfer surfaces.

Many methods have been proposed to predict the formation of CaCO_3 . However, they are all based on the thermodynamic equilibria of H_2CO_3 and are alkalinity corrected for temperature and dissolved solids (ionic strength). The more commonly used equations or indices are the Ryznar Stability Index (RSI) [6] and the Langelier Saturation Index (LSI) [7]. The LSI is defined as:

$$\text{LSI} = \text{pH} - \text{pH}_S \quad (\text{Eq 1})$$

where pH is the actual measured value in the water, and pH_S is the pH of saturation calculated from the expression:

$$\text{pH}_S = (\text{p}K_2' - \text{p}K_{\text{SP}}') + \text{pCa} + \text{pAlk} \quad (\text{Eq 2})$$

where K_2' is this apparent second dissociation constant of H_2CO_3 , K_{SP}' is the apparent solubility product of CaCO_3 , pCa is $-\log_{10} (\text{Ca}^{2+})$ in moles per litre, and $\text{pAlk} = -\log_{10}$ [total alkalinity] in equivalents per liter. The complexity of Eq 1 and 2 has been reduced to nomographs [8]. The RSI is an empirical expression:

$$\text{RSI} = 2\text{pH}_S - \text{pH} \quad (\text{Eq 3})$$

where pH and pH_S have the same meaning as previously described. Interpretations of LSI and RSI values are listed in Table 1.2.

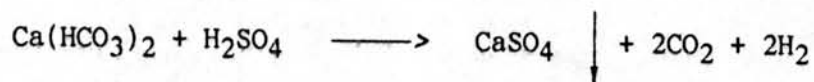
These indices indicate only the tendency for CaCO_3 to deposit, not the rate or capacity for deposition. Also, these values do not take into account the tendency for CaCO_3 to supersaturate, its rate of formation, or whether the water contains any inhibitor to prevent deposition.

Calcium carbonate formation can be controlled by adding acids or specific chemicals tailored to inhibit its formation

Table 1.2 Prediction of water characteristics by LSI and RSI

Index		Tendency of water
LSI	RSI	
2.0< 4	Heavy scale forming, nonaggressive
0.55-6	Slightly scale forming and mildly aggressive
06-6.5	Balanced or at CaCO ₃ Saturation
-0.56.5-7	Nonscaling and slightly aggressive
-2.0> 8	Undersaturated, very aggressive

or modify the crystal lattice. Sulfuric acid (H₂SO₄), which inexpensive, is most often used. Other acids, such as HCl, citric, or sulfamic acid (NH₂SO₃H), are also suitable. Acid addition produces salts that are more soluble than CaCO₃. These salts can reach saturation and must be controlled to prevent precipitation on heat transfer surfaces:



Calcium carbonate precipitation can also be inhibited by

chemical treatment. A cost-effective group of materials is the polymeric inorganic phosphates. This class of compounds includes the salts of pyrophosphate, tripolyphosphate, and hexametaphosphate. Approximately 1 mg/l of active material can stabilize 44 times the CaCO_3 equilibrium saturation. This concentration is well below the stoichiometric values required for complexing calcium hardness and is termed threshold treatment. At this concentrations, the polyphosphates inhibit the crystallization of CaCO_3 crystallites by suppressing both nucleation and crystal growth. The poly phosphates are partly adsorbed on the surface of growing crystals and partly included in incipient crystal nuclei. A disadvantage of the polyphosphates is heir ability to hydrolyze or revert to PO_4^{3-} ions, which have no scale-inhibiting properties.

Other phosphate compounds found to be effective belong to the class known as phosphonates. Two of the more common compounds are AMP (nitrilo tris (methylene phosphonic acid)) and HEDP (1-hydroxyethylidene-1, 1-diphosphonic acid). Threshold treatment inhibitor concentrations range from 0.25 to 0.5 mg/l, although higher concentrations are often used. The compounds AMP and HEDP have greater hydrolytic stability than the polyphosphates. It should be noted that AMP will degrade in the presence of Cl^- to PO_4^{3-} ions. The addition of Zinc ions (Zn^{2+}) significantly stabilizes the AMP molecule while ill maintaining its control over CaCO_3 scale. Although HEDP is less affected by Cl^- ion than AMP, at least 50 % of the HEDP is degraded

to PO_4^{3-} at residual chlorine concentrations of 0.2 to 5 mg/l [9].

Organic polymers have also been found to be effective CaCO_3 inhibitors. This include polycarboxylates, such as polyacrylates, polymethacrylates, polymaleates, and their copolymers. Treatment levels are higher than the phosphorus-bearing materials, usually in the range of 2 to 4 mg/l. The molecular weights of these polymers should range from 1000 to 10000 amu for effective scale control.

The polymers adsorb onto the CaCO_3 crystal structure, limiting the growth of CaCO_3 and ultimately limiting scale formation. These polymer are more frequently considered dispersants. They are CaCO_3 scale by maintaining small particles distorted crystalline material in suspension. Bifunctional compounds are a recent development for CaCO_3 control. Phosphinocarboxylic acids contain both organic phosphorus and carboxylic acid groups [10]. Simple molecules combining both the phosphone and carboxylic groups have also emerged and are very effective CaCO_3 inhibitors [9]. However, these bifunctional compounds may be more expensive than traditional low molecular weight polymers, polyphosphates, or phosphonates.

Calcium sulfate can exit in various forms in cooling water systems, the most common form being gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). The hemihydrate and anhydrous forms are much less common. Their

solubilities as a function of temperature are shown in Fig. 1.4.

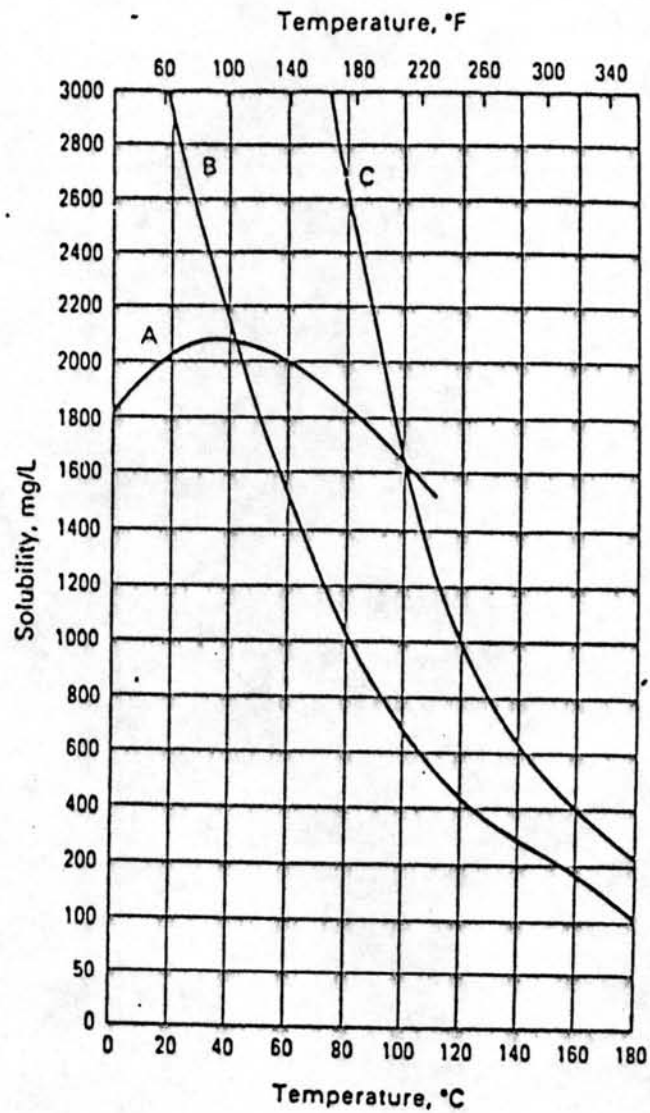


Fig. 1.4 Solubility of three forms of CaSO_4 versus water temperature. A, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$; B, anhydrous CaSO_4 ; C, hemihydrate ($\text{CaSO}_4 \cdot 1/2 \text{H}_2\text{O}$)[11].

Because $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is more soluble than CaCO_3 by at least a factor of 50, it will precipitate only after the latter scale have been formed, within the normal pH range of 7 to 9. This phenomenon provides the basis for H_2SO_4 addition to control CaCO_3 in recirculating cooling water systems. The normal upper limit for calcium and sulfate concentration in the absence of an inhibitor is expressed by:

$$[\text{Ca}^{2+}] \cdot [\text{SO}_4^{2-}] = 500\,000 \quad (\text{Eq } 4)$$

where the bracketed values are the ionic concentrations expressed in milligrams per litre.

Calcium sulfate scale can be most effectively controlled with polyacrylates [12], their co-polymers, and phosphinocarboxylates [10]. As with CaCO_3 , excellent calcium scale control is achieved with polymers having low molecular weights in the range of 1000 to 10 000 amu. Concentrations of 1 to 2 mg/l can increase CaSO_4 solubility by a factor of 20. This is similar to maintaining the $[\text{Ca}] \cdot [\text{SO}_4] > 10^7$ compared to 500 000 in the absence of chemical treatment. These polycarboxylates are stable over a wide range of pH and temperature. The basic mode of inhibition is through a combination of threshold crystal distortion and dispersancy, mechanism that prevents or delays precipitation.

Another chemical that controls CaSO_4 precipitation

efficiently is the phosphonate AMP. Infact, the family of aminophosphonates has been found to be extremely effective. The level of AMP needed is approximately 0.5 mg/l.

Calcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$) scale has become more common in recirculating cooling water systems. Increasing pH, calcium concentration, and phosphate addition from chemical treatment have provided the potential for this deposit to form on heat transfer surfaces. Other water sources have also contributed to increased level of phosphate. Makeup waters obtained from agricultural run off and partly treated sewage can have high levels of PO_4^{3-} ions (at least 10 mg/l).

The solubility of $\text{Ca}_3(\text{PO}_4)_2$ decreases with increasing pH. It is essentially unaffected over normal temperature ranges (about 25° to 75 °C, or 75° to 165 °F). These deposits are usually amorphous and eventually transform to a more crystalline hydroxyapatite- $\text{Ca}_3(\text{PO}_4)\text{OH}$. Because of the low solubility of $\text{Ca}_3(\text{PO}_4)_2$ (about 10^{-30}), deposits can easily form in waters containing 5 mg/l PO_4^{3-} ions and 300 mg/l of Ca^{2+} ions at pH 7 to 7.5. The scale forming tendency of $\text{Ca}_3(\text{PO}_4)_2$ is a complex function of pH, calcium hardness, PO_4^{3-} concentration, ionic strength, and temperature. Rule-of-thumb relationships between these variables do not exist. Also in the absence of any phosphate deposit, the PO_4^{3-} ions can contribute to the corrosion inhibition of carbon steel.

Calcium phosphate is an extremely difficult scale to inhibit. Intensive research has brought forth new chemistry to control this tenacious deposit. These new inhibitors include acrylic-hydroxypropylacrylate co-polymer [13], styrene sulfonic acid-maleic acid co-polymer [14], and phosphino/acrylic acid-organo-sulfonic acid co-polymer. They function by markedly modifying the morphology and size of $\text{Ca}_3(\text{PO}_4)_2$ deposit while also acting as a dispersant to prevent adherence of $\text{Ca}_3(\text{PO}_4)_2$ to heat transfer surfaces. Normal concentrations of these co-polymers are 10-15 mg/l under conditions of moderate calcium hardness (about 500 mg/l as CaCO_3) and 10 mg/l of PO_4^{3-} ions at pH 8 to 8.5. Increasing any of these parameters will require an increase in polymer concentration.

Silicate Scales. Calcium silicate (CaSiO_3) and magnesium silicate (MgSiO_3) scales tend to develop under more alkaline cooling water conditions, in which the pH is approximately 8.5 or greater. These scales are very tenacious, dense, and difficult to remove from heat transfer surfaces. Although the solubility of silica (SiO_2) increases with pH, the solubility of the alkaline silicates decreases with increasing pH.

An upper limit for SiO_2 concentration is 150 mg/l in the recirculating water, although other factors affect this value. Magnesium silicate can precipitate on heat transfer surfaces with magnesium concentrations as low as 50 mg/l and 150 mg/l SiO_2 . A rule-of-thumb pseudosolubility product of

$[Mg] \cdot [SiO_2] \leq 8400$ has been developed (bracketed values are in milligrams per litre). The addition of chemical treatment as a preventive measure is essentially nonexistent. The most effective method of control is to keep the SiO_2 concentration in the recirculating cooling water below the 150 mg/l limit.

Fouling Deposition

Fouling deposits Water-borne deposits, commonly known as foulants, are loose, porous, insoluble materials suspended in water. They include such diverse substances as particulate matter scrubbed from the air; migrated corrosion products; silt, clays, and sand suspended in make-up water; organic contaminants (oils); biological matter; floc carryover from clarifiers; and such extraneous materials as leaves, twigs, and wood fibers from cooling towers. Fouling interferes with the flow of cooling water as compared to the reduction in heat transfer caused by barrier scales: However, fouling can reduce heat transfer efficiency because of plugging of the exchanger. Thus, adequate water flow through the tubes is essential.

High flow rates (1.5 to 2.5 m/s, or 5 to 8 ft/s) can sweep away ordinary deposits, but low flow rates (less than 0.6 m/s, or 2 ft/s) cause the suspended foulants to drop out and deposit. Regions of low velocity include shell-side coolers, compressor jackets, water boxes, and cooling tower basins.

Mechanical methods can be used to reduce fouling. In once-through cooling systems, coarse filters (bar screens, trash racks, traveling screens) are used to remove large debris. Fine filtration is not practical. This is not case with open recirculating systems. When the makeup water contains an appreciable concentration of suspended matter, it is advantageous to use side-stream filtration. In general, passing a few percent of the recirculating water through the side-stream filter will reduce the suspended solids loading 80 to 90% .

Another affective mechanical method used to control foulants is to pass scrapers, brushes, or balls through the heat exchanger tubes, wiping them free of deposits. This technique is most frequently used in power utility surface condensers or other critical exchangers.

Chemical treatment has also been found to be an effective control method. Synthetic polymers are the chemicals more commonly used to disperse foulants. Polyacrylates, polymaleates, partially hydrolized polyacrylamides, and their co-polymers constitute the majority of dispersant chemicals. The most important aspect of these materials is their molecular weights. An effective dispersant has a molecular weight of 1000 to 10 000 amu the same range as for scale control. Concentrations of a few milligrams per litre are required in open recirculating systems, but lower levels are normally used in once-through systems.

Natural dispersants, such as tannins, lignin sulfonate, and carboxymethyl cellulose, are occasionally used, but they are not as the synthetic polymers. The natural materials require higher concentrations to produce good dispersion of foulants, may not be cost effective, and may contribute to foaming. The synthetic polymers are not as easily degraded by biological organisms as the natural polymers are.

Increasing the molecular weight of the synthetic polymers into the million range changes the characteristics of the treatment from dispersion to flocculation. These high molecular weight polymers consist of polyacrylamines, polyamines, or polyacrylates and their various co-polymers.

Fouling is controlled by agglomeration of the suspended solids into nonadherent larger particles. To settle deposits, the polymers are usually added to concentrations of 0.2 to 0.5 mg/l to clarifiers or thickeners. Similar concentrations are used in open recirculating systems. However, the deposit will accumulate in low-flow or stagnant areas in the recirculating systems. Normally, heat transfer will not be seriously reduced, because of the low bulk density of these deposits. Buildup of sludge in the cooling tower basins will necessitate periodic cleaning.

Objectives for This Study

The objectives of this work are described in the following:

1. Study of the calcium carbonate stabilizer of chemicals for cooling water treatment.
2. Study of the calcium phosphate stabilizer of chemicals for cooling water treatment.
3. Use the chemicals in the results of objectives 1 and 2 for experiments in cooling tower system model.