CHAPTER 2

THEORETICAL CONSIDERATION AND LITERATURE REVIEW

Corrosion Control

Aqueous corrosion has been shown to consist of electrochemicalprocesses Thedetrimental effects of these processes in cooling water environments can be significantly reduced by various methods, such as designing systems with more corrosion resitant materials, applying protective coatings (paints, epoxy), and using sacrificial anodes (cathodic protection) and chemical treatments.

For chemical treatment or corrosion inhibitor programs to be effective, they must protect all exposed metal from corrosive attack, must be effective at low concentration, must not cause deposits on the metal surface, must remain effective under broad range of pH, temperature, water quality and heat flux, must prevent scale formation and disperse deposits, and must have minimal toxicological effect when discharged. Economics should also be considered when assessing the merits of a chemical treatment program. In once-through cooling systems, protection must be achieved with a few milligrams per liter, or the cost may be prohibitive. For these types of systems, use of more corrosion-resistant alloys is often a more economical approach to corrosion control. With respect to open recirculating cooling systems, chemical addition to the make-up water can be in the range of 10 to 50 mg/l (active). cost is not as prohibitive, because of the recycling of the water system, which also includes the inhibitor. Closed recirculating cooling water systems require high active treatment levels (in the range of several thousand milligrams per litre). These systems have very small water losses.

Inhibitors can be broadly classified according to the rate process being controlled. Anodic inhibitors suppress anodic reactions: that is, the rate of metal ions being transferred into the aqueous environment is reduced. Cathodic inhibitors impede the cathodic reaction-for example, oxygen reduction reaction. Mixed inhibitors hinder both reactions.

Inorganic inhibitors usually affect the anodic process. Rapid suppression of general corrosion occurs. However, when this inhibitors are below a critical concentration, they can stimulate localized pitting attack and therefore must be used with caution.

Cathodic inhibitors reduce corrosion primarily by interfering with oxygen reduction reaction. This family of inhibitors decreases general corrosion and does not stimulate pitting attack. When the anodic and cathodic reactions are both affected by the chemical treatment, a mixed mode of inhibition is in effect.

The performance of an inhibitor can be assessed by its effectiveness in reducing the corrosion rate. This is generally expressed as a rate of thinning or penetration in microns per year or mils per year.

The current approach to cooling water treatment is toward the more alkaline or high-pH conditions. This was not always the case. Historically, acid treatment was widely used to prevent scale deposition on heat transfer surfaces. The system pH was slightly acidic (pH 6.5-7.0), and corrosion was controlled by using highly effective anodic inhibitors, the most effective being chromates.

Anodic Inhibitors

Chromates are highly effective in protecting ferrous and many nonferrous alloys against corrosion. The protective film is formed on ferrous metals through the oxidation of iron to form a mixed oxide ($Cr_2O_3 + Fe_2O_3$) [16].

There is a critical chromate concentration that is necessary for protection, because this inhibitor is sensitive to aggressive ions, such as Cl^- and SO_4^{2-}. Below this minimum, severe pitting attack can occur even though uniform corrosion is low. Above the minimum chromate concentration, local attack is arrested, producing excellent overall protection. Normal control concentrations of chromate for proper steel protection require a high initial dosage of 500-1000 mg/l to meet the Cl^- and

SO_4^{2-} demands, followed by a reduction in concentration to a maintenance level of 200-250 mg/l. There is no discernible change in corrosion protection within normal bulk water temperatures (38^o to 65^oC, or 100^o to 150^oF) and pH ranges (6 to 11).

When chromates are used at low concentrations of approximately 15-25 mg/l, their mode of inhibition is cathodic [17]. Steel protection is provided in conjunction with the dissolved oxygen in the water to produce the protective oxide layer of γ-Fe_2O_3. The reduction product of chromate (Cr_2O_3) does not become part of the protective oxide. The pH range remains the same as for high concentration-pH 6 to 11. Low levels of chromate are insensitive to electrolyte concentration.

Nitrites. Sodium nitrite ($NaNO_2$) is an anodic inhibitor and requires a critical concentration for the protection of steel. Nitrites are extensively used as inhibitors in closed recirculating systems. The level of inhibitor depends on the aggressive species in solution. Sulfate ions interfere with nitrite protection to a greater extent than Cl^- ions. Treatment level should be at least the concentration of $NaNO_2$ required to produce a weight ratio of 1 with aggressive ion concentrations ($[NaNO_2]/[NaCl + Na_2SO_4] = 1$). This concentration is normally in the range of 500 to 750 mg/l at pH above 7.5. Nitrite may contribute to pitting of carbon steel if the concentration falls below this critical level.

Nitrites are easily oxidized to nitrates in open recirculating cooling water systems and therefore are not suitable. However, when formulated with borax, nitrites are excellent corrosion inhibitors for closed systems. The borax buffers the water to a pH above 8.5. Dosage levels for the borax-nitrite systems are 1500 to 2000 mg/l, with a nitrite concentration near 800 mg/l. It should be noted that NO_2^- ions are nutrients for some species of bacteria, which can oxidize the NO_2^- ions and render the treatment ineffective, producing slime deposits and a low pH. Biocides (isothiazolinone) are often used in conjunction with borax-nitrite programs for optimum protection.

Molybdates have been available for corrosion protection for over 50 years, but have never been widely used. Molybdates are classified as anodic inhibitors. In waters having moderate Cl^- concentration (200 mg/l), the level of sodium molybdate (Na_2MoO_4) needed for protection is at least 1000 mg/l. In dilute electrolytes, the concentration can be reduced to 150 mg/l. Normal treatment pratices consist of combinations molybdates with other inhibitors to produce synergistic treatments. This reduces the high level of molybdate ions (MoO_4^{2-}) needed when used alone. Combinations with zinc salts; phosphogenates (AMP and HEDP); inorganic phosphate nitrites; and carboxylates, such as long-chain acrylates and azoles (benzo- or tolyltriazoles) have been shown to be effective in controlling corrosion of multimetal systems [18].

Sodium molybdate is a nonoxidizing inhibitor and requires a suitable oxidizing agent to augment the inhibitor and to impart a protective film. In aerated systems, the most abundant oxidizer is oxygen. Any of the above combinations are applicable except nitrites (see the section "Nitrites" in this article). A wide range of ratios have been used in specific formulations. A typical treatment consists of MoO_4, HEDP, zinc, and benzotriazole in a 3:3:1:1 weight ratio [18].

The use of molybdates in closed systems requires an oxidizing salt, such as $NaNO_2$. The optimum composition for the Na_2MoO_4:$NaNO_2$ system consists of a 60:40 weight ratio of the two salts [18].

Molybdate treatments have minimal pH dependcy and can be used over a pH range of 5.5-8.5. They are sensitive to electrolyte concentration and are adversely affected by aggressive ions, such as Cl^- and SO_4^{2-}, when used alone. temperature dependency is minimal. molybdate treatments are known to inhibit both pitting and differential aeration attack. The precipitation of calcium molybdate ($Ca(MoO_4)$) is a concern in waters with moderate-to-high calcium hardness.

The mechanism by which molybdates inhibit the corrosion of ferrous metals is uncertain and complex. Simplistically, when iron corrodes, MoO_4^{2-} ions, in conjunction with other anions, adsorb to form a nonprotective complex with Fe^{2+}

ions. Because of dissolved oxygen or other oxidizers in the water, some of the Fe^{2+} ions are oxidized to the ferric (Fe^{3+}) state, and the ferrous-molybdate is transformed to ferric-molybdate, which is both insoluble and protective in neutral and alkaline waters.

Phosphates. Sodium phosphate (Na_3PO_4) is an anodic inhibitor and is effective in the presence of oxygen. Its protective properties toward steel are a function of pH. The monosubstituted phosphate (MH_2PO_4, where M is a metal) is the least protective, but the trisubstituted phosphate (M_3PO_4) is the most protective. Use of phosphate as a corrosion inhibitor should be relegated to more alkaline environments ($pH > 8$).

In open recirculating waters, phosphate treatment levels should be 15 to 20 mg/l. At lower concentrations of few milligrams per liter, PO_4^{3-} ions will cause pitting attack. The oxygen content of the system is primarily for the ability of the phosphate to inhibit steel [21]. The dissolved oxygen produces a defective thin film of γ-Fe_2O_3. The PO_4^{3-} ions fill in the voids and accelerate film growth. These plugs prevent any further diffusion of Fe^{2+} ions from the metal surface. The primary reactant responsible for steel inhibition is oxygen, which forms the thin oxide film.

Inhibition by PO_4^{3-} ions is sensitive to electrolyte concentration; Cl^- ions can promote pitting attack. Because the protective oxide film contains voids and other inclusions, Cl^- ions are easily asorbed to soluble complexes. Hydrolysis of these complexes produces acid domains, which leads to localized acidic attack. Film breakdown is a function of the aggressive ion concentration, but film repair will depend on PO_4^{3-} level and oxygen concentration.

Overall inhibition by PO_4^{3-} ions is sensitive to water quality and pH. There is minimal temperature sensitivity. One word of caution regarding PO_4^{3-} ions as steel corrosion inhibitors: With waters of high calcium hardness, the potential for deposit formation increases with hardness, phosphate level, pH, and temperature. These deposits will stimulate crevice (underdeposit) corrosion. need for an inhibitor to prevent calcium deposits becomes exceedingly more important as cooling waters increase in cycles of concentration and pH.

Cathodic Inhibitors

Cathodic inhibitors suppress the corrosion rate reducing the effectiveness of the cathodic process. They do not cause intense local attack and are generally considered to be safe inhibitors. Cathodic inhibitors are not as effective as the anodic inhibitors.

Precipitating inhibitors fall under the domain of a cathodic inhibitor. They produce insoluble films on the cathodic under conditions of locally high pH and isolate the cathode from the solution. Calcium bicarbonate ($Ca(HCO_3)_2$) will react with the alkaline medium at the cathode to form $CaCO_3$. The increase in alkalinity is due to the oxygen reduction process, generating OH^- ions:

$$(CaHCO_3)_2 + OH^- \longrightarrow CaCO_3 + HCO_3^- + H_2O$$

At the appropriate pH, $CaCO_3$ will precipitate to form a hard, smooth deposit that prevents oxygen from diffusing onto the metal surface. The tendency of a water to form a $CaCO_3$ deposit is given by the LSI

Zinc ions are used to achive a general reduction in corrosion by precipitating as zinc hydroxide ($Zn(OH)_2$) at the cathodic due to locally elected pH. Zinc is usually combined with chromates, phosphonates or polyphosphates. The durability of $Zn(OH)_2$ is tenuous at best. Although not normally used alone in cooling systems, zinc is synergistic when combined with other inhibitors as part of a multicomponent treatment program.

Zinc causes rapid development of a protective film over the metal surface. Above pH 7.5, the solubility of zinc is rapidly reduced to a few tenths of 1 mg/l. Its solubility can be significantly enhanced when combined with phosphonates or with some of the polymers used for $Ca_3(PO_4)_2$ control.

Polyphosphates are widely used cathodic inhibitors. They have been in use for more than 40 years and are among the most economical of all inhibitor treatments. Sodium salts of the polyphosphates are normally used for corrosion control. They exit as linear polymers having the general structure shown in Fig. 2.1.

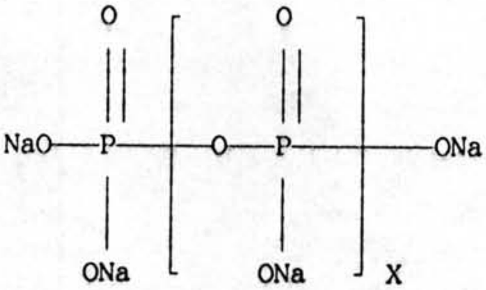

Fig. 2.1 General structure of sodium polyphosphate. x=0, sodium phosphate; x=1, sodium pyrophosphate; x=2, sodium tripolyphosphate; x=12 to 14 , sodium polyphosphate

The lower members of series having x equal to or less than 2 are crystalline in nature, that is, x=0 orthophosphate; x = 1, pyrophosphate; x = 2, tripolyphosphate. Higher members of the series are glassy and have no definitive structure.

Varying the ratio of $n\,Na_2O : m\,P_2O_3$ will produce species of different chain lengths and physiochemical properties, even though the inhibitive action of these polyphosphates is not significantly altered. The pH of the environment directly affects the protective properties of the phosphates. Orthophosphate inhibits corrosion in a more alkaline environment than pyrophosphate does. The crystalline phosphates protect steel at higher pHs the glassy phosphates, which function better near neutral pH. Normal concentrations in recirculating waters are 15 to 20 mg/l. The pH should be maintained in the range of 6.5 to 7.5 if steel and copper alloys are both part of the system metallurgy.

The polyphosphates are relatively insensitive to electrolyte concentrations, but do require an increase in dosage level with an increase in water corrosivity. They are effective inhibitors in controlling galvanic attack between two dissimilar metals [20], but do not prevent deposition of cathodic species on the more sctive metal, that is, copper deposition on steel.

Divalent metal ions, and Ca^{2+} in particular, are needed with the polyphosphates for effective inhibition of steel. The ratio of Ca^{2+} ions concentration to polyphosphate concentration should be at least 0.2, and preferably 0.5. The protective film develops through the formation of a positively charged colloidal complex that migrates to the cathode, forming an amorphous protective barrier. The cationic complex is accounted for by assuming that the calcium intercalates the polyphosphate chains. The colloidal particles are the result of numerous cathonic complexes loosely knit one to another through the

Ca^{2+} ions. The polyphosphates will revert to PO_4^{3-} ions, which is a potential scale in the presence of Ca^{2+} ions and alkaline pH.

The phosphonates differ from the polyphosphates by a direct bond formation between the phosphorus and carbon atoms, rather than an oxygen-phosphorus bond in the polyphosphate. This linkage creates greater hydrolytic stability, which reduces the problem of reversion common to the polyphosphates. Two classes of materials are extensively used: AMP and HEDP. Their structures are shown in Fig. 2.2 and 2.3.

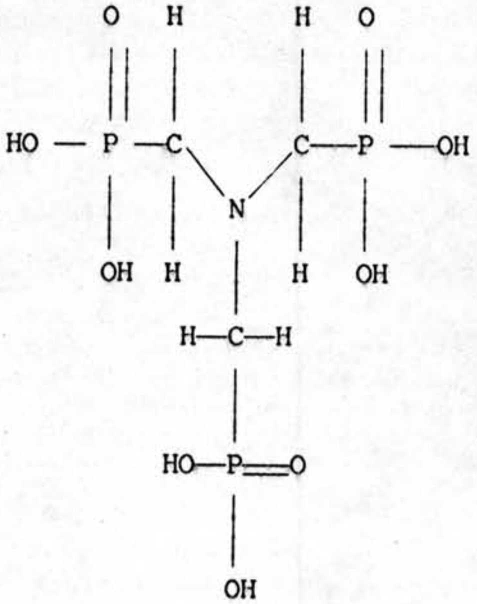

Fig.2.2 Structure of AMP

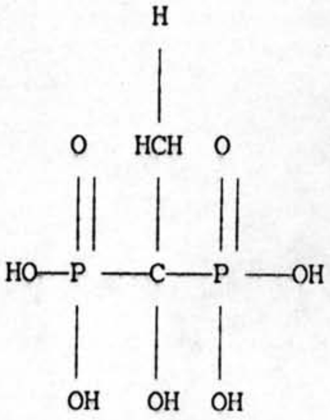

Fig.2.3 Structure of HEDP

When used alone, both compounds are marginally good steel inhibitors, especially at high pH (pH 8.0). They protect ferrous metals through a mixed mode of inhibition. Incipient local attack occures but is rapidly arrested. Normal treatment levels are in the range of 15 to 20 mg/l.

The hydraulic stability of the phosphonates eliminates the problem of $Ca_3(PO_4)_2$ deposition in moderately to highly alkaline waters. However, AMP will degrade in the presence of chlorine, producing PO_4^{3-} ions, and therefore should not be fed concurrently. The phosphonates from very stable complexes with a variety of metal ions and thus accelerate their corrosion. Increase attack occurs on nonferrous alloys, especially the copper-base alloys. The addition of zinc significantly suppresses this antagonistic attack. Calcium phosphonate deposits will form in moderate-hardness high-alkaline waters, that is, 400 to 500 mg/l calcium hardness at pH 8 to 8.5. These deposits can be controlled with some of the new polymers available for $Ca(PO_4)_3$ control.

The phosphonates are sensitive to overall water quality. The protection afforded to carbon steel decreases with increasing aggressive ion concentration. Sensitivity to temperature is also exhibited. The major difference between AMP and HEDP is that the letter resists oxidation to a greater extent and can therefore be used in the presence of chlorine.

Multicomponent Systems

Cooling water formulations containing mixtures of inhibitors usually offer increased protection to ferrous metals. Such mixtures are synergistic in their action. Many combinations have been developed to achieve enhanced protection under a wide variety of plant operating conditions. Heavy-metal formulations containing zinc and/or chromate have been widely used in industry, where environmentally acceptable, particularly for severe corrosion problems. Nonheavy-metal treatment programs (no zinc or chromium) are receiving increased attention because of government discharge restraints. Complex blends of PO_4^{3-}, polyphosphate, phosphonate, copper corrosion inhibitor (see the section "Copper Inhibitors" in this article), and $Ca_3(PO_4)_2$ dispersants are probably the most widely used multicomponent inhibitors.

Zinc chromate ($ZnCrO_4$) is one of the most effective multicomponent treatments. It inhibits carbon steel corrosion by stifling the oxygen reduction reaction and is therefore classified as a cathodic inhibitor. Both components of this formulation-low-level zinc and low-level chromate-are also cathodic inhibitors. As little as 5% of either component will show significant synergistic action to ferrous metals, although at least 20% of each ingredient appears to be optimum [21]. Both zinc and chromate exist as individual species in solution without the formation of a specific compound or intermediate.

The effect of zinc addition (5 to 10 mg/l as Zn^{2+} ion) to low-level chromate (up to 20 mg/l of CrO_4^{2-}) is synergistic and significantly reduces local attack. This formulation has broad applicability to multimetal systems. It is capable of protecting copper-base metals, aluminium alloys, and galvanized steel. The protection afforded by $ZnCrO_4$ to these multimetal systems is the reduction of general attack and the prevention of galvanic attack due to the reduction of noble metal ions on more active base metal.

Normal concentrations are approximately 10 mg/l of each constituent. The treatment program is insensitive to normal operating temperatures and overall water aggressiveness. Therefore, $ZnCrO_4$ has broad application to a multitude of water compositions and levels of aggressiveness in addition to a wide range of operating temperatures. The pH of the system can range from 5.5 to 7.5, with a pH of 7 being most acceptable. Even after major upsets due to pH excursions, the protective film is rapidly reestablished. However, there are some disadvantages to this treatment. Zinc chromate has no threshold-inhibitive effect on hardness scales. It lacks dispersion action to keep the metal surfaces free of deposits and debris, and pH excursion above 7.5 will cause precipitation of zinc to form insoluble basic zinc salts.

Zinc Chromate/Phosphonate. The disadvantages of $ZnCrO_4$ formulation are circumvented by the addition of such a phosphonate as AMP. Approximately 5 mg/l of the phosphonate supplements the $ZnCrO_4$ program to threshold treatment to prevent $CaCO_3$ and $CaSO_4$ scales. It can extend the pH range up to 9 because of the increased stability the phosphonate gives Zn^{2+} ions. the phosphonate adds detergent power to the system,'flushes away suspened solids, and helps keep the metal surface clean.

Zinc chromate is not a nutrient for biological growth; this simplifies biological control. The Zn^{2+} ions, which are stabilized at high pH, also improve the resistances to phosphonate degradation. All of the advantages of $ZnCrO_4$ are maintained:rapid film formation, insensitivity to electrolyte concentration, and insensitivity to temperature.

Zinc Polyphosphate. the addition of zinc to the polyphosphates does not appreciably change the general nature of the polyphosphates. This system retains its insensitivity to electrolyte concentrations, its threshold inhibition of $CaCO_3$ and $CaSO_4$, its ability to protect ferrous and nonferrous metals, and its detergent properties. Zinc polyphosphate inhibitors also enable multivalent metal ions to form positivity charged colloidal complexes.

Zinc increases the rate at which the protective film is formed on the metal surfaces [22]. This rapid protective film formation improves the general corrosion protection to the system. It is also synergistic in combination with polyphosphates. The amount of treatment needed using a zinc/polyphosphate inhibitor combination is less than that required for the polyphosphates alone.

The mode of inhibition is cathodic, similar to the polyphosphates in calcium-containing waters. The zinc accelerates film formation, restraining attack until a thin, tencious, durable film is developed. The deposition of zinc phosphate ($Zn_3(PO_4)_2$) does not seem to be involved in the inhibition process.

Approximately 10 to 20% Zn is usually incorporated into the polyphosphate for synergisism. Beyond this level, little improvement is observed. Maintenance concentrations are usually 10 mg/l as polyphosphate. Good practice requires a dossage of two to three times the maintenance level as a pretreatment to the system for a short period of time, that is, less than 1 week. A pH range of 6.8 to 7.2 is required for good control. This limination in pH is necessary to prevent excessive attack on copper-base alloys (the lower the pH, the greater the attack on copper). Sensitivity to bulk water temperature is minimal.

Zinc Phosphonates. The combination of zinc with phosphonates provides significantly improve protection compared to phosphonates alone. The addition of zinc make this formulation synergistic in its protection to carbon steel.

Good corrosion control is attained by using 20 to 80% Zn, with 30 to 60% being optimum [23]. Overall treatment levels are 8 to 10 mg/l phosphonate with 2 to 3 mg/l Zn^{2+} ions. The need for zinc becomes paramount in the presence of copper-base alloys. When used alone, the phosphonates are aggressive to copper and form a strong copper-phosphonate complex. Zinc negates this antagonisyic effect by forming a stronger and more stable complex, significantly reducing attack on the alloys. The effectiveness of the zinc-phosphonate combination is due to increased cathodic protection. The zinc effectively counteracts the anodic character of the phosphonates through the formation of a phosphonate-zinc complex, which is cathodic compared to the phosphonate alone.

Due to this complex, broad pH application becomes possible. The zinc phosphonate treatment can be used over a pH range of 6.5 to 9. Zinc is held in solution at these more alkaline pH levels, and protection actually improves with an increase in pH.

Little sensitivity is shown with increased salt or electrolyte concentration, and temperature effects are minimal. Thus, the zinc-phosphonate systems can be used over a wide range of water quality, at high bulk water temperatures (70^{o} to $75^{o}C$, or 160^{o} to $170^{o}F$), and with pH levels up to 9.0.

Degradation of phosphonates to PO_4^{3-} ions by chlorine is significantly reduced with a phosphonate/zinc system, and the latter can be used in cholrine environments because of diminished chlorine demand. The zinc stabilizes the complex, preventing the deterioration of the carbon-phosphorus bond in the oxidizing environment.

Nonheavy-Metal Systems. Many combinations of building blocks are currently being used in nonheavy-metal formulations. Some of the systems in use include combinations of the phosphonates, AMP/HEDP; polyphosphate/polyphosphonate mixtures, polyphosphate/HEDP; polyphosphate or phosphonate/orthophosphate; and polyphosphate or HEDP/PO_4^{3-}. These systems are synergistic in protecting carbon steel. They combine the many advantages of the individual components, including:

- Complex formation with calcium and numerous polyvalent metal cations required to form the protective film over the metal surface. The polyphosphates still form the colloidal species for cathodic protection, and the phosphonate serves as a cathodic polarizer.
- Threshold inhibition of slightly soluble inorganic salts, such as $caCO_3$ and $CaCO_4$.
- Detergent and dispersive action on surface deposits.

Most nonheavy-metal treatments for carbon steel function best in more alkaline or elevated pH systems. Waters are less corrosive but more prone to form scale or deposit.

Therefore, good scale control is absolutely necessary. These treatments are generally not as effective as heavy-metal formulations. However, because of the less corrosive nature of the recirculating cooling system, good overall protection can be achieved. More care and attention are required to operate these nonheavy-metal treatments because they are less tolerant of system upsets and function under more contained ranges of water corrosivity, pH, and temperature.

The AMP/HEDP nonheavy-metal inhibitor pair is classified as a cathodic inhibitor. A critical AMP/HEDP ratio of 1.5:1 is needed for optimum carbon steel protection. Performance improves with pH and should be used in systems having a pH of at least 7.5. The combined phosphonate program is not as sensitive to temperature as the individual components, nor is it adversely affected by high levels of Cl^- and SO_4^{2-} ions.

Normal treatment levels of at least 15 mg/l total phosphonate can be used to achieve good protection (<75 μm/yr, or 3 mils/yr). Adequate pretreatment of at least two to three times normal concentration for 1 week is required before reducing the concentration to a maintenance level. With good pH control, normal treatment levels can be reduced and still achieve the desired corrosion protection. Concern over attack on copper-base alloys still exists such that the addition of a special copper inhibitor is highly recommended.

Polyphosphate/HEDP. The second non heavy metal system-polyphosphate/HEDP-is also cathodic in nature while being synergistic in protecting carbon steel. Approximately 40 to 80% by weight of the polyphosphate is needed for good protection of carbon steel. Corrosion control of approximately 50 μm/yr (2 mils/yr) can be achieved with 15 mg/l total phosphate content. the sensitivity of Polyphosphate/HEDP to pH is minimal over the range of pH 6 to 8. Temperature sensitivity is minor. Good corrosion control is achieved at bulk water temperatures exceeding 60^oC (140^oF). As with the AMP/HEDP system, sensitivity to water aggressiveness is not a major concern. The antagonistic effects of Cl^- and $SO_4{}^{2-}$ ions are subdued by this treatment program.

Treatment levels are approximately 15 to 20 mg/l, which can be reduced if the system is pretreated at two to three times maintenance concentration for at least 1 week. Attack on copper-base alloys is reduced compared to the AMP/HEDP system; however, as with the combined phosphonate system, there is a need for a specific copper inhibitor. Concern over reversion still exists, because the polyphosphates are subject to hydrolysis. The $PO_4{}^{3-}$ ions generated will improve the overall corrosion protection, assuming $Ca_3(PO_4)_2$ precipitation is controlled.

The polyphosphate/PO_4 combination functions in a mixed mode. The cathodic portion comes from either the polyphosphate or phosphonate (HEDP), while the anodic portion derives from the PO_4^{3-} ion. The addition of PO_4^{3-} improves protection to carbon steel through a synergistic interaction with either polyphosphate [14] or phosphonate. The level of polyphosphate or phosphonate is not critical and can range from 20 to 80%. The corrosion rate of carbon steel can be esaily controlled to 25 μm/yr (1 mils/yr) with 15 to 18 mg/l total phosphate.

This system is applicable over a broad pH range of 6.0 to 8.5. There is little sensitivity to pH. The lack of sensitivity to pH refers only to corrosion control, and the inhibitors remain active in solution. The formation of a $Ca_3(PO_4)_2$ precipitate is prevented by the addition of an appropriate additive that inhibits its growth and adherence to the metal surface.

Sensitivity to temperature is also minimal. The inhibitor pair has applicability to very hot system having bulk water temperatures as high as 70^{o} C (160^{o} F). Reversion of the polyphosphate molecules to PO_4^{3-} will be accelerated at the higher temperature, but will also enhance overall protection due to the inhibitive activity of its product (PO_4^{3-} ions).

The system is moderately sensitive to aggressive ions, specifically Cl^-, that can promote pitting attack. Because PO_4^{3-} is an anodic inhibitor there is a critical concentration that must be maintained that is a function of the electrolyte.

Treatments containing polyphosphate will revert, to PO_4^{3-}, and a sufficient amount of a $Ca_3(PO_4)_2$ inhibitor should be present to suppress its formation.

Attack on copper-base alloys is not a major concern when polyphosphates are used. However, the phosphonate can be aggressive to copper-base alloys. The addition of a specific copper inhibitor is recommended.

Copper Inhibitors

Most of the steel inhibitors that have been discussed exert some degree of control over corrosion of copper-base alloys. However, system upsets, such as pH excursions and process attacks, can dissolve copper into the cooling water, where it can interfere with steel protection. concentrations of at least 0.1 mg/l can deposit on steel conduits, accelerating localized attack. Ancillary inhibitors are available that are very effective in controlling corrosion of copper-base alloys and preventing galvanic deposition or dissolved copper onto ferrous metals.

Three specific inhibitors have been extensively used: mercaptobenzothiazole (MBT), benzotriazole, and tolyltriazole. Mercaptobenzothiazole is an extreamly effective inhibitor for copper-base alloys. Its inhibitive properties are attributed to formation of an adherent protective film on the metal oxide surface. The inhibitor reacts with the metal surface to form a chemisorbed barrier. The initial corrosion product of Cu^+ ions reacts with the MBT molecule to form a 3-dimensional complex of Cu(I) MBT. Rate of film growth is rapid, reaching a self-limiting thickness within a short period of time.

Mercaptobenzothiazole is susceptible to oxidizing agents, such as air, chlorine, and ultraviolet light from sunlight, that can degrade the molecule into a disulfide having no inhibitory properties. This degradation occurs only to the molecule in solution, not the complex on the metal surface. Because of the sensitivity of MBT toward chlorine, the inhibitor should be used only if no chlorine residual is present. Thus , MBT should not be added to open recirculating cooling water systems, in which continuous chlorination is often practiced.

Cupric ions can be effectively inhibited from cathodically depositing onto more active metals, such as steel and aluminium, by reacting with MBT in a 1.2 molar ratio. In the absence of complicating factors, such as copper concentrations exceeding 0.1 mg/l in the cooling water or a chlorine residual, the concentration of MBT required for good copper inhibition is approximately 4 m/l. A feeding procedure based on 3 mg/l, followed by 1 mg/l addition 12 hrs later, has been very sucessful.

Benzotriazole and tolyltriazole function similarly in controlling copper corrosion. Structurally, tolyltriazole differs from benzotriazole in that the former has a methyl group attached to the benzene ring. Both materials behave similarly in cooling water, reacting with the metal surface to produce a three-dimensional chemisorbed layer.

The azoles are classified as cathodic inhibitors because they adsorb at cathodic sites and interfere with the oxygen reduction reaction. These molecules are more resistant to oxidation than MBT. In the presence of chlorine, 1-chlorobenzotriazole (or 1-chlorotolyltriazole) is propably formed, having minimal inhibitory properties. Upon dissipant of residual chlorine, the chloro-compound reverts back to the active azole. Chlorination does not affect the integrity of the complex on the metal surface.

The azoles can deactivate dissolved copper in cooling water systems and prevent its deposition onto steel or active metals. A 2:1 molar ratio of inhibitor to copper ions is required, similar to the MBT reaction.

The concentration of azoles necessary for copper inhibition is approximately 1 to 2 mg/l in the absence of any residual chlorine. The optimum practice is pretreat the system with two to three times normal concentration for 1-2 days, then control at a maintenance dosage. Under chlorination conditions, the azole should be fed after the dissipant of residual chlorine. If continuous chlorination is practiced and cannot be changed to intermittent practice, the level of treatment should be increased to 4 to 5 mg/l. In the presence of continuous chlorination, over all copper corrosion protection will be less than with intermittent chlorination.