Education Institute for

Equipment & Process Design

Corrosion Inhibitor

Corrosion Mechanism Review

Chapter 1, section 8 of this manual should be reviewed as background for understanding the mechanisms of corrosion inhibition discussed in this section.

As a brief review, corrosion reactions of metals in water are electrochemical in nature. They consist of two separate reactions:

- An anodic reaction, in which metal is dissolved to produce metal ions in solution and corrosion products, either on the metal surface or dispersed in the water; and
- A cathodic reaction in which dissolved oxygen is reduced to form hydroxide ions, or in acid solutions hydrogen ions are reduced to hydrogen gas.

Thus, when steel (iron) corrodes in water, the anodic reactions are:

$$2Fe^0 = 2Fe^{+2} + 4e^- \qquad (4\text{-}22)$$

$$2Fe^{+2} + 4OH^- = 2Fe(OH)_2\downarrow \qquad (4\text{-}23)$$

$$4Fe(OH)_2 + O_2 + 2H_2O = 4Fe(OH)_3\downarrow \qquad (4\text{-}24)$$

The corresponding cathodic reaction is the reduction of oxygen,

$$O_2 + 2H_2O + 4e^- = 4OH^- \qquad (4\text{-}25)$$

or in acid solution, the reduction of hydrogen ions:

$$2H^+ + 2e^- = H_2\uparrow \qquad (4\text{-}26)$$

These reactions involve a transfer of electrons. This means that an electric current, called the corrosion current, must flow from anodes to cathodes through the metal surface, and back to the anodes through ions in the water, as shown in figure 1-12 in chapter 1.

Polarization

Any process that interferes with either the anodic or the cathodic reaction, or with both reactions, will reduce or stop the flow of current and hence reduce or stop corrosion. Two naturally occurring processes that limit the flow of corrosion current are called polarization and passivation.

Most corrosion reactions in water systems are self-limiting. The products of the anodic and cathodic reactions – ferrous and ferric hydroxides at the anodes, and hydroxides and calcium carbonate at the cathodes – tend to shield the metal surface and prevent ready access of water containing dissolved oxygen. This process, called polarization, limits the rate of the cathodic reaction and hence reduces the corrosion rate.

For this reason, initial high corrosion rates tend to slow down and approach a limiting value that depends upon the configuration of the surface and the composition of the water. High flow velocities and/or high turbulence can overcome this polarization effect. Corrosion rates then increase because corrosion products cannot accumulate to help shield the metal surface.

Passivation

As explained in chapter 1, elements that are high in the galvanic series (Table 4-1) are so reactive that they cannot exist as the free elements under atmospheric conditions. Sodium and potassium, for example, react violently with water. These are, in effect, simply extremely rapid corrosion reactions.

However, other elements close to the top of Table 4-1, such as magnesium, aluminum and zinc, that are also very reactive as free elements, are stable in contact with air and water, and are widely used as materials of construction. The difference is that these elements form stable oxide films that effectively seal the surface and prevent all contact with water and air. This process is called passivation. The dull gray film seen on galvanized steel that has been exposed to air is a good example of a naturally formed passive film. Stainless steels earn that title by forming a very thin, mostly invisible film of chromic oxide on the surface that prevents corrosion.

An important property of naturally formed passive films is that they are self-repairing. If the film is damaged, a small amount of corrosion occurs to reform the film, and the surface again becomes passive. This is true as long as the environment does not attack the oxide film. Thus, galvanized steel is commonly used for cooling tower construction. However, the pH of the water must not be allowed to range below about 6.5 or above about 8.5. Outside of this range, the oxide film dissolves and the zinc coating corrodes away. Similarly, stainless steels are stable in sulfuric acid, which provides an oxidizing atmosphere, but they corrode readily in hydrochloric acid, a reducing acid.

The terms passivation and passive films refer to protective films formed by direct reaction of a metal with its environment, without any external additives. However, these terms are also used to describe protective films formed by corrosion inhibitors (section 5.10) and by oxygen scavengers (chapter 3).

CORROSION INHIBITORS

Types of Inhibitors

Corrosion inhibitors are simple inorganic or organic chemicals that, when added to water at mg/L dosage levels, interfere with the electrochemical corrosion reactions on steel, copper and other metals, and dramatically reduce corrosion rates.

Specific corrosion inhibitors are discussed in the following sections. Corrosion inhibitors as a group fall into three general classifications:

- Reactive inhibitors chemically react with (corrode) the metal surface to produce a protective film (sometimes called a passive film) that is chemically bonded to the surface and contains both oxidized metal and some form of the inhibitor. These films are quite stable. They are resistant to velocity and turbulence effects and usually provide some residual corrosion protection for a time if inhibitor feed is discontinued for any reason. Chromate and nitrite on steel, and various azoles on copper, are typical examples of reactive corrosion inhibitors.
- Precipitating inhibitors provide corrosion protection by precipitating an inert barrier layer on the metal surface. These layers are not chemically bonded to the surface, but when well formed, they can be quite resistant to flow velocity and turbulence. Zinc, forming zinc hydroxide films, and phosphate, forming ferric and calcium phosphates, are typical examples of precipitating inhibitors.
- Filming inhibitors are chemicals, such as amines, organic acids and other polar organic molecules that form chemical or electrostatic bonds with the metal surface, without actually corroding the surface. Many of these molecules contain a charged ionic group at one end that attaches to the surface, and a hydrophobic group that extends outwards and helps to keep water away from the surface. Filming inhibitors are very useful, but they are the least stable to flow velocity and turbulence. Filming amines used in boiler condensate corrosion control are examples of filming inhibitors.

Corrosion inhibitors are also classified in terms of the corrosion reaction that they inhibit:

- Cathodic inhibitors interfere with the cathodic reaction, reduction of oxygen (equation 4-25). As explained in chapter 1, corrosion reactions in cooling water environments are under cathodic control. That is, the rate of the cathodic reaction, governed by the rate at which dissolved oxygen can diffuse to the metal surface, controls the overall corrosion rate. By reducing the available cathodic area, cathodic inhibitors proportionally reduce the overall corrosion rate.
- Anodic inhibitors suppress the anodic reaction, that is, metal ions going into solution (equation 4-22). Anodic inhibitors are very effective in controlling general corrosion, because they directly protect the corroding sites. However, anodic inhibitors can also stimulate pitting attack if maintained below a critical concentration. Since the overall corrosion reaction is under cathodic control, reducing the available anodic area does not directly reduce the corrosion rate; it simply concentrates the attack on any available anodic sites. As explained more fully in chapter 1, this can lead to serious localized pitting corrosion. For this reason, anodic inhibitors are also called "dangerous inhibitors". Minimum concentrations of anodic inhibitors required for good protection have been determined experimentally for each product. These concentrations will vary somewhat with water quality. High dissolved solids and low alkalinity waters will require higher inhibitor dosages for safe protection.
- Mixed inhibitors are blended products that suppress both the anodic and cathodic reactions. This is a desirable way to gain the benefit of the good protection of anodic inhibitors with added safety from the overall reduction in corrosion rate from cathodic inhibitors. Many commercial corrosion inhibitors are formulated in this way.
- General inhibitors, or filming inhibitors as above, cover the entire surface of the corroding metal through the development of adsorbed protective films. Sometimes these films are polymeric in nature.

Inhibitor Selection

Many different corrosion inhibitors, alone and in various combinations, are available to provide protection to the engineering alloys used in cooling water treatment. However, selecting the proper inhibitor is not always a simple matter. A good understanding of the system, including water chemistry, operating routines, system metallurgy and critical heat exchangers, is required, along with good product line knowledge. See the discussion of system surveys at the end of this chapter, for more on this important subject.

Following are some general criteria for corrosion inhibitor selection:

- The inhibitor must protect all exposed metal from corrosive attack.
- The inhibitor must be effective at low, cost-effective dosage levels, and at reasonable cycles of concentration and pH, in the site-specific water.
- The inhibitor should be effective under a broad range of operating conditions, i.e. temperature, pressure, flow rate, process demands and timing, etc. to allow for system variability.

- The inhibitor must not form deposits other than inhibiting films on the metal surface.
- The inhibitor should not stimulate microbiological activity, or the microbiological treatment program must be designed to control this problem.
- The inhibitor should have minimal toxicological effects when discharged, and it should be acceptable in the receiving waterway or sewer. In some cases, specific treatment of the blowdown water may be required.

Many different corrosion inhibiting chemicals can be used alone, or in various synergistic combinations, to provide multimetal protection in cooling water systems. Following are brief descriptions of the most widely used cooling water corrosion inhibitors.

Chromate

Chromate is included in this manual because of its historical significance. Before about 1985, chromate was used extensively as a corrosion inhibitor. It is a reactive, anodic inhibitor, extremely effective over a wide range of operating conditions, especially in open cooling tower systems when blended with cathodic inhibitors such as zinc or polyphosphate.

However, in the late 1980s, chromate was banned because of its toxicological impact on the environment (chromate is a known carcinogen). With chromate no longer available for open system use, other inhibitors had to be developed to provide needed corrosion protection. Newer products are more environmentally friendly, and can be equally effective.

Some tightly regulated closed systems still use chromate-treated water, particularly in severe service applications and where the water is very corrosive. In such cases, operating personnel are required to maintain control of the entire inventory of treated water, and to report any losses or discharge to both state and federal environmental authorities.

Orthophosphate

Phosphate-based chemicals are the most widely used corrosion inhibitors in open cooling water systems. Trisodium orthophosphate, $Na_3(PO_4)_2$, is simply the trisodium salt of orthophosphoric acid, H_3PO_4. The disodium and monosodium salts are also available. These are widely used for pH and alkalinity control in boiler water treatment as well as in open cooling water systems (see chapter 3).

The orthophosphate anion is the simplest species in this family of corrosion inhibitors. It is an anodic, precipitating inhibitor, that effectively inhibits corrosion of low carbon steel by precipitating ferric phosphate, $FePO_4$, at anodic sites. Good corrosion control can be achieved above pH 7.5, especially in soft water systems. Below this pH, orthophosphate is less effective because ferric phosphate becomes soluble. Phosphate chemistry is sensitive to water quality, especially chloride content. High concentrations of chloride (above 300 mg/L) reduce the efficiency of orthophosphate-based corrosion inhibitors by promoting localized pitting attack.

When orthophosphate can be used, protective film formation is very rapid and tenacious. Orthophosphate works synergistically with other inhibitors to provide excellent corrosion protection, similar to chromate. A major concern with orthophosphate is the potential for calcium phosphate precipitation in high pH and hard waters (see chapter 1).

It is often suggested that orthophosphate should also act as a cathodic corrosion inhibitor, because tricalcium phosphate, $Ca_3(PO_4)_2$, becomes very insoluble at the higher pH levels generated at cathodic sites (chapter 1). In fact, this is probably correct. However, tricalcium phosphate precipitates slowly, as the end product of a chain of complex intermediate phosphates, while ferric phosphate precipitates quickly at the anodic sites. Therefore, in a corroding system, any cathodic inhibition achieved by orthophosphate is overshadowed by the immediate anodic protection provided by ferric phosphate. In a well-protected system, where little or no corrosion takes place, tricalcium phosphate, if it is allowed to form, will provide additional cathodic corrosion protection over time.

Many large municipalities add roughly 1 mg/L of orthophosphate to their water supplies, in order to precipitate small amounts of lead dissolved from old piping systems. It is important to consider this in planning a chemical treatment program. When concentrated in a cooling tower, makeup water phosphate can be a significant factor in both corrosion control and potential precipitation of calcium phosphate scale.

Polyphosphates

Phosphate chemistry is a complex subject that is beyond the scope of this manual. Briefly, phosphates can polymerize, just like many organic molecules, to form several different classes of polyphosphate compounds. The compounds most often used in cooling water treatment include:

- The dimer, tetrapotassium pyrophosphate.
- The trimer, sodium tripolyphosphate.
- Sodium hexametaphosphate.

Polyphosphates are classified as cathodic precipitating inhibitors. They react with calcium under high pH conditions at cathodic sites (chapter 1) to form a thin, protective film of calcium polyphosphate. Polyphosphates provide corrosion protection for carbon steel in an effective pH range from 6.5 to about 8.0. A minimum of about 50 mg/L calcium hardness is essential if polyphosphates are to function as corrosion inhibitors. Other than hardness, polyphosphates are relatively insensitive to water quality. Sometimes, polyphosphates are combined with zinc, another cathodic corrosion inhibitor, to improve performance (zinc polyphosphate and zinc hydroxide are both insoluble in the normal open cooling water system pH range.

A concern with polyphosphates is that they revert (depolymerize) to form orthophosphate and increase the potential for calcium phosphate precipitation. Reversion rates are increased by low pH and high temperature. Pyrophosphate is the most stable of the common polyphosphates, while tripolyphosphate is the least stable. Conveniently, the potassium salt, tetrapotassium pyrophosphate, $K_4P_2O_7$, is very soluble, so that liquid formulations containing pyrophosphate as a corrosion inhibitor can easily be made.

Because of their ability to form soluble complex ions with calcium, polyphosphates are sometimes used as chemical softening agents in domestic water supplies.

Phosphonates

Organic phosphate compounds are called phosphonates. Phosphonates are distinguished from inorganic polyphosphates in that all phosphonates contain direct carbon-phosphorus bonds. Phosphonates are primarily used in cooling water treatment to control calcium carbonate scale (section 6.0), but they also have corrosion-inhibiting properties.

Phosphonates belong to the class of compounds known as general precipitating inhibitors that protect both anodic and cathodic sites. The compounds that precipitate to form protective films are calcium and iron salts. The composition of the film depends upon the phosphonate, the specific blended formulation in use, the composition of the circulating water and operating conditions.

A problem with all phosphonates is that like polyphosphates, they decompose over time to form orthophosphate. As a group, phosphonates are more stable than inorganic polyphosphates, but decomposition rates increase with temperature and with low pH. Phosphonates are also attacked by oxidizing biocides (chlorine and bromine compounds). All of these factors must be considered when designing chemical treatment programs including phosphonates.

- HEDP (1-hydroxethylidene 1,1 diphosphonic acid), when used alone, is a relative poor corrosion inhibitor. However, when formulated with zinc, it provides good protection. The effective pH range is 7 to 9. HEDP requires at least 25 to 50 mg/L calcium (as carbonate) in the water for film formation. However, at calcium levels above about 300 mg/L as calcium carbonate, HEDP can precipitate as a calcium-HEDP salt. This can lead to loss of both mineral scale and corrosion control, and to formation of calcium-HEDP scale. Polymers can be added to the formulation to help prevent precipitation of the calcium phosphonate salt. HEDP is more resistant to attack by chlorine than is AMP (below), but not as resistant as PBTC.

AMP [aminotri(methylenephosphonic) acid] also is a relative poor corrosion inhibitor when used alone. In the presence of zinc, excellent corrosion protection on carbon steel can be achieved, especially in soft water. AMP contains a nitrogen atom to which three methlyene phosphonate groups are bonded. These nitrogen bonds weaken resistance to chlorine, so that AMP is rapidly degraded. The effective pH range is 7 to 9. AMP is more tolerant of high calcium levels than is HEDP, but in high hardness water, AMP can form a complex and precipitate a calcium-AMP salt that can add to system scale.

PBTC (2-phosphonobutane, 1,2,4-tricarboxylic acid) is one of the most stable of the phosphonates. It will not degrade in the presence of typical chlorine levels in cooling water systems. When used with zinc, PBTC can provide excellent carbon steel corrosion protection. It also has good tolerance towards calcium, so that calcium phosphonate precipitation is not a potential problem.

HPA (hydroxyphosphonic acid) is a phosphonate that was specifically designed for carbon steel corrosion protection, rather than calcium carbonate scale control. When used alone, HPA requires calcium in the water for effective protection of carbon steel. However, in combination with zinc, HPA provides excellent corrosion control on carbon steel in soft water. HPA degrades easily with low levels of chlorine in water, but the manufacturer claims that this reaction can be controlled by adding monoethanolamine (MEA) to the formulation.

Bricorr 288C, (a phosphonocarboxylic acid) provides corrosion protection similar to HPA, but with much improved resistance to chlorine oxidation.

All of the above phosphonates are chelants and will complex with zinc, which helps in providing good corrosion control to carbon steel. However, due to their chelant nature, phosphonates can attack copper. To avoid this problem, specific copper corrosion inhibitors should always be included when phosphonates are used in systems containing copper components.

Zinc

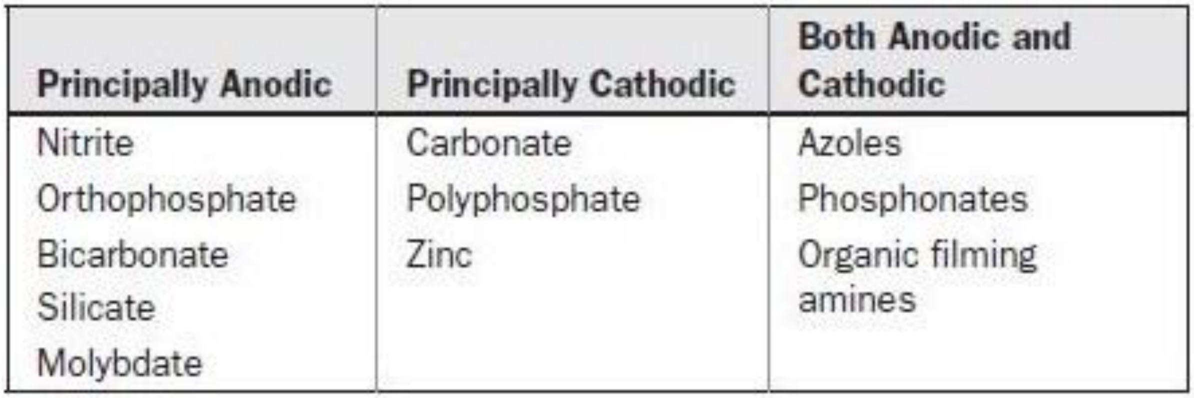
Zinc is a mediocre corrosion inhibitor for carbon steel when used alone. However, it is a valuable synergistic addition to almost all other corrosion inhibitors in open cooling water systems, providing an added level of cathodic, precipitation-type protection to reduce the overall corrosion rate. The precipitated film is zinc hydroxide or a complex zinc hydroxycarbonate, depending upon the circulating water composition and temperature. These films form preferentially at cathodic sites because of local high pH conditions (chapter 1).

Some of the benefits of adding zinc to any corrosion inhibitor formulation are :

- Improved protection.
- More tenacious films.
- Faster film formation.
- Lower required concentrations of other inhibitors, compared to use without zinc.

Zinc therefore is always used in formulations with other corrosion inhibitors. The effective maximum pH for zinc-containing systems without stabilization is 7.5 Above pH 7.5, zinc hydroxide precipitates in the bulk water, so that corrosion protection is lost.

However, this problem is easily solved by incorporating zinc-stabilizing polymers in the formulation. These polymers help to prevent zinc hydroxide from precipitating in the bulk water, but allow it to form under the higher pH conditions that exist at cathodic sites. With polymers present, zinc-containing corrosion inhibitors can be used up to about pH 8.5. Effective zinc levels are between 0.5 and 5.0 mg/L as Zn. Proper selection and dosage of the stabilizing polymer is critical for the success of these programs. Zinc is rarely used in closed systems.



Principally Anodic	Principally Cathodic	Both Anodic and Cathodic
Nitrite	Carbonate	Azoles
Orthophosphate	Polyphosphate	Phosphonates
Bicarbonate	Zinc	Organic filming amines
Silicate		
Molybdate		