

Corrosion

Introduction

Corrosion of metals in cooling and boiler water systems occurs in differing forms depending on the condition of the water, temperature, flow rate, etc. This chapter discusses types of corrosion, the causes and mechanisms involved, and methods used to inhibit corrosion.

After reading this chapter, you should have a firm grasp of the mechanical aspects of corrosion, along with a basic understanding of corrosion inhibition in water systems. Keep in mind that all of the information contained in this section will prove useful in designing a chemical approach to corrosion inhibition.

The Electrochemical Nature of Corrosion

Corrosion is the natural process of deterioration of metals and alloys in a corrosive environment. This is a very broad definition, but corrosion occurs in a wide variety of forms, both in pure metals and in alloys. This discussion considers primarily the two most frequently occurring forms of corrosion, general corrosion and pitting. General corrosion is the wasting away of a metal or alloy in a corrosive environment, resulting in an actual decrease in the thickness or size of the original metallic structure. This wasting away occurs relatively uniformly over

the surface exposed to the corrosive environment. Pitting is a form of localized corrosion in which a small portion of the metallic structure is corroded at a rate much faster than the bulk of the structure.

Metals such as steel and copper and alloys such as brass and stainless steel appear to be fairly rugged and able to withstand a great deal of physical abuse. This is not true when these metals are surrounded by a corrosive environment. They can be quickly reduced to thin, rusty or oxide-encrusted specimens. To put it another way, these metals always have a tendency to return to their naturally occurring forms.

Metallic elements such as iron, copper, zinc and nickel occur naturally in the form of oxides, sulfides and carbonates. In metal making, this natural process is reversed and the metallic element is separated from its oxide. This requires a great deal of energy, as anyone who has seen a blast furnace can tell you. The resulting metal or alloy is in a high-energy state and, under the right conditions, it will attempt to return to its more natural, lower-energy, reacted state. A detailed corrosion study of a piece of metal is the study of how this happens, the rate at which it happens and what causes it to happen. There are several conditions that must be met before these reactions can occur.

- 1. The metal, in this case, iron, must be reactive. It must be inherently unstable in the metallic form, thereby tending to corrode.**

2. The metal must be in contact with an electrolyte. An electrolyte is a solution, usually aqueous, which can conduct electric current and support ionized species.

3. The electrolyte must contain dissolved species. This can be either dissolved gases, such as oxygen or chlorine, or dissolved ions, such as the hydrogen ion, which acts as an oxidizing agent.

4. The kinetics of the situation (the rate at which the corrosion reactions can occur) must be rapid enough to be of practical significance.

The first requirement, that the metal must have sufficient reactivity, is exhibited by metals such as iron, copper and steel. They readily corrode under the proper conditions. On the other hand, gold and platinum are more noble metals and do not react readily with their environment. Without the presence of dissolved gases or minerals in an electrolyte, such as water, even highly reactive metals do not corrode. Water contains many types of minerals.

Electrode Potentials and the Galvanic Series

Corrosion reactions are a combination of oxidation and reduction reactions.

Oxidation is the electrochemical process by which an element or species loses electrons and increases its valence state. A metal transforming to a metal ion with the simultaneous loss of an electron is an example.



Reduction is the electrochemical process by which an element or species acquires one or more electrons. Thus reducing its valence. The transformation of hydrogen ions to atomic hydrogen is an example.



When reactions of these types occur, they never occur in isolation, only in pairs or combination. In fact, the oxidation process, which produces more electrons, depends on the simultaneous consumption of those electrons by a reduction reaction. If no reduction reaction is available, no oxidation occurs. In these cases, the species which undergoes a reduction reaction is called the oxidizing agent.

The quantitative study of oxidation/reduction reactions has resulted in two useful concepts:

1. Oxidation - reduction potentials (which apply to elements and compound)
2. Galvanic series (which applies to alloys in their environments)

Oxidation-Reduction Potentials

The Table below is a listing of some useful oxidation-reduction potentials.

These values represent the thermodynamic tendency for the indicated reaction

to occur on a relative basis. All potential values are compared to an arbitrary value of 0.00 volts which is assigned to the hydrogen oxidation reaction. The more negative a value, the more likely the reaction will proceed in the direction shown in the Table. Thus we see that zinc oxidation:



is more likely to occur than iron oxidation



which, in turn, is more likely than hydrogen oxidation



Some other generalizations drawn from the standard oxidation reduction potential table are:

1. Oxygen is a stronger oxidizing agent than hydrogen ion.
2. Iron is more reactive than lead, copper or silver.
3. Gold is very unreactive.

The Galvanic Series

The following Table is a simple version of the galvanic series of alloys

in seawater. Because electrode (oxidation/reduction) potentials only apply to pure elements and true compounds, another system was developed to compare the relative reactivity of alloys in an environment. This series has the added advantage of allowing you to predict the galvanic behavior of certain alloy pairs in an environment.

If a pair of alloys listed in the series are coupled, the alloy higher in the list will be corroded more rapidly than if it were uncoupled, and the alloy lower in the series will be protected, or corrode more slowly than if it were uncoupled. The table shows why alloys of aluminum and magnesium are galvanically coupled to steel to protect the steel. Coupling steel to copper, brass or stainless steel accelerates the corrosion of steel.

Corrosion Reactions and Corrosion Mechanisms

Nearly all corrosion reactions of practical interest are oxidation-reduction reactions. The oxidation portion of the reaction results in the actual metal loss, while the reduction portion of the reaction drives the whole process. The most common corrosion reaction is the rusting of steel in water:



In neutral or alkaline solution the individual reactions are:



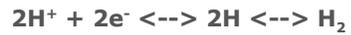
The mechanism of this reaction is complex. The oxygen attacks the surface of the iron and oxidizes it, releasing ferrous and hydroxyl ions into the surrounding water. A secondary reaction then takes place, further oxidizing the ferrous ion to the ferric ion. This species forms an insoluble precipitate of iron hydroxide that tends to stick onto the iron surface.

The initial stages of the reaction occur quite rapidly. The oxygen has free

access to the surface, where it diffuses and reacts. As ferrous and hydroxide ions build up near the surface, the oxygen near the surface becomes depleted, and the reactions begin to slow down. As the reactions proceed, ferric hydroxide forms a gel near the surface and further restricts oxygen diffusion to the surface. This is commonly observed in the form of barnacles. Eventually the reaction slows to an equilibrium rate governed by the rate at which oxygen diffuses through the rust. Over a period of time, the corrosion rate of the iron gradually decreases and levels out.

Common Corrosive Agents

Most, but not all, of the common corrosive agents encountered in industrial waters are gases. The reactions of importance are:



Other corrosive agents occur in industrial waters, although infrequently.

Among these are the ferric ion (Fe^{+3}), sulfide ion (S^{-2}), bromine (Br_2)

and cupric ion (Cu^{+2}).

Corrosion Product Films

All corrosion reactions produce corrosion by-products. In some environments, these products are very soluble and no films actually form on the surface of the corroding metal. A corrosion process characterized by the absence of a tenacious film is called active corrosion. In other media, corrosion products form insoluble hydroxides, carbonates, oxides and sulfates. Some are loose and porous, allowing diffusion to and from the metal surface. These types of films do not protect surfaces from further corrosion.

A few films which form as a result of corrosion are very adherent, tight, and nonporous. These are considerably more protective toward further corrosion, primarily because they limit access of corrosives to the metal

surface.

Some alloys are inherently unreactive. Aluminum and stainless steels form corrosion product films of mixed oxides that are so non-reactive and that completely protect the base metal after a short period of active corrosion. These alloys are passive, and the films are called passive films.

Types of Corrosion

General Corrosion

General corrosion is the most common type of corrosion. It is defined as the uniform loss of metal from the entire exposed surface of the metal.

Pitting Corrosion

Pitting is a type of localized corrosion in which a small portion of the exposed surface experiences very high corrosion rates resulting in small holes in the metal surface. This type of corrosion usually occurs when general corrosion rates are low. Pitting is especially dangerous because the metal loss rates can be very high. The result is unexpected failures in pipes and tubes.

Crevice Corrosion

Crevice corrosion is another form of localized corrosion. It occurs in crevices on metal structures. Corrosion materials build up in the space of the crevice and create a highly localized and very corrosive environment. Certain anions, such as chlorides, promote the hydrolysis reactions that cause the problem.

Underdeposit Corrosion

This is a special type of crevice corrosion where the crevice or space is caused by a deposit on the metal surface. Scale, corrosion products or a variety of other debris can cause deposits under which accelerated corrosion occurs. After deposits are formed, it is difficult to stop underdeposit corrosion, because the deposits make it difficult to get corrosion inhibitors to the metal surface suffering the high corrosion rates. Another form of underdeposit corrosion common in open recirculating cooling systems is caused by the attachment of biomasses to metal surfaces. The biomass produces by-products that are corrosive to most metals and are held next to the metal surface by the biomass.

Galvanic Corrosion

When dissimilar metals are connected in an electrolytic solution under the proper conditions, one metal will experience accelerated corrosion. The alloy highest in the galvanic series will corrode faster. The relative areas of the two alloys are important. If the area of the more active alloy is small compared to the area of the noble metal, then the severity of the galvanic attack will be greater.

Impingement

Impingement is an accelerated form of corrosion that occurs when a metal surface, covered by a protective film, is damaged by mechanical or hydraulic wear or abrasion. Mechanical abrasion will remove protective films, but the effect of high fluid velocity, intense turbulence and cavitation can accelerate this process. These effects are most often observed at inlets to heat exchanger tubes, at piping elbows, in piping downstream of pumps, and on pump impellers. Copper and copper alloys are especially sensitive to impingement.

Operational Factors Affecting Corrosion Rates

Temperature

As a general rule, increasing temperature increases corrosion rates. This is due to a combination of factors- first, the common effect of temperature on the reaction kinetics themselves and the higher diffusion rate of many corrosive by-products at increased temperatures. This latter action delivers these by-products to the surface more efficiently.

Occasionally, the corrosion rates in a system will decrease with increasing temperature. This can occur because of certain solubility considerations. Many gases have lower solubility in open systems at higher temperatures. As temperatures increase, the resulting decrease in solubility of the gas causes corrosion rates to go down.

pH

Corrosion rates almost always increase with decreasing pH (increasing acidity). This is a direct result of increasing the concentration of an aggressive ion (H^+) and increasing the solubility of most potentially corrosive products.

Oxygen Concentration

Oxygen's role in corrosion is as an aggressive gas or oxidizing agent. As its concentration increases, corrosion rates increase until the rates

of diffusion to the surfaces reach a maximum. The same principles apply to most other oxidizing agents, such as Cl_2 , H^+ , Br_2 .

Fluid Velocity

The dependence of corrosion rate on fluid velocity is complex. In general, the higher the velocity, the higher the corrosion rate. At very low velocities, even zero, there are diffusion effects that can cause corrosion. As fluid velocities increase from stagnant to moderate values, the corrosion rates increase. Then, as the limit of diffusion at a particular temperature is reached, further increases in velocity have little effect on the corrosion rate. At some point, however, the velocity reaches such high values that the surface film of the metal begins to be damaged. At these velocities, the corrosion rates resume increasing with the higher velocities.

Suspended Solids

An increase in suspended solids levels will accelerate corrosion rates. These solids include any inorganic or organic contaminants present in the water. Examples of these contaminants include clay, sand, silt or biomass.

Corrosion Inhibitors

To inhibit corrosion, small amounts of corrosion inhibitors can be added to water systems and process streams to reduce corrosion rates to acceptable values. In general, corrosion inhibitors incorporate themselves into corrosion product films in such a way as to increase the film's capacity to prevent corrosion. The process of corrosion inhibition is related to the metal surface and the processes occurring in waters on that surface. The polar nature of some molecules promotes adsorption, but the idea that corrosion inhibitor films act as barriers is erroneous. The adsorption of these molecules is accompanied by the companion process of desorption. An inhibitor molecule usually is in constant motion, being adsorbed and desorbed between the fluid and the corrosion product film. The rate of adsorption onto the surface is dependent on the nature of the molecule, as well as the concentration of the inhibitor in the fluid. The same is true for the process of desorption. It is important in inhibitor treatment to maintain a sufficient concentration of the molecule in the fluid so that the adsorption rate at least equals the desorption rate. This process is commonly referred to as passivation.

Types of Corrosion Inhibitors

Organic

These materials are characterized by high molecular weight structures,

incorporating nitrogen or phosphorous groups. They are usually highly polar molecules.

- **Phosphate Esters**
- **Phosphonates**

Inorganic

Salts of some metals and amphoteric elements act as corrosion inhibitors.

Quite often these materials have tenacious film-forming or passivation effects. In some instances, they react with the metal surface.

- **Chromate Salts**
- **Zinc Salts**
- **Molybdate Compounds**
- **Phosphates**
- **Nitrite Salts**
- **Silicate Compounds**

Corrosion in Recirculating Cooling Systems

A recirculating cooling system is a perfect environment for corrosion. All of the conditions for producing significant levels of corrosion are present. Reactive metals, in contact with electrolyte-containing corrosive elements, accelerate the reactions. Recirculating systems have several complicating factors likely to aggravate the corrosion problems even further:

1. **Heat Transfer:** Heat exchanger surfaces corrode more rapidly than other metal surfaces in the system.

2. **Fouling and Scale Formation:** Not only can fouling cause underdeposit corrosion problems, but it may frequently hinder corrosion control procedures by shielding the metal surface from access to chemical corrosion inhibitors.

3. **Biofouling:** Biomasses can form on metal surfaces. Accelerated corrosion can occur underneath these biomasses due to the operation of corrosive by-products resulting from metabolic processes. The mass itself can hinder the action of detergent materials or chemical corrosion inhibitors by presenting a physical barrier between those materials and the metal surfaces requiring protection.

4. **Physical Process Conditions:** High fluid velocity, very low fluid velocity, excessive turbulence and similar physical process characteristics may have a strong influence on the corrosion problems in a system. Very high fluid velocity in some condenser tubes may cause a mildly corrosive water to inflict severe damage on copper alloy tubes. Low flow rates, especially if they result in dead areas, prevent the efficient distribution of chemicals such as chlorine, corrosion inhibitor or scale preventative.

5. **Control Upsets:** Most cooling water towers are partly dependent on parameters that are frequently under automatic or semiautomatic control. If that control fails, then the corrosion rates can increase drastically. For example, if acid addition to adjust pH is out of control, the result is very high corrosion rates. A wide variety of upsets will directly or

indirectly effect corrosion rates.

6. Process Leaks: If a leak develops in a cooling water system, the results can be disastrous. Corrosion rates can increase at dramatic rates. Leaks must be detected and stopped as quickly as possible.

Solutions to Corrosion Problems in Water Systems

Economic considerations are normally the primary influence on decisions that are made when choosing a corrosion control program. The economic benefits of controlling corrosion in process water systems include savings on equipment losses, savings in production downtime from unexpected corrosion failures, energy savings on heat transfer surfaces, and savings on the treatment of aqueous plant effluents. One way to solve corrosion problems in industrial water systems (seldom selected because of its high cost) is the engineering solution. This might come in the form of substituting corrosion-resistant alloys for mild steel in areas that are subject to corrosion. Sometimes coatings of various types are used to protect steel from potentially corrosive waters. A more practical solution involves the increasing use of nonmetallic materials, such as plastics, in water handling systems.

Another method of solving corrosion problems is to make operational changes. For example, the exclusion of a corrosion stream into the water system by segregating it may solve a problem, or at least isolate it to a part of the

plant where it may be economically handled. Many times, however, this is not a feasible solution.

But by far the most widely used form of corrosion control in industrial water systems is a combination of control and the use of specialty chemical corrosion inhibitors. For many years this was accomplished in cooling systems through the use of a simple, low-cost inhibitor package whose major active ingredient was sodium chromate. These treatments had the capability to effectively control corrosion (producing corrosion rates of 1 mpy or less) while at the same time reducing microbiological growth and eliminating scale formation on heat transfer surfaces. Legislation has reduced the amount of heavy metals allowed in many plant effluents, making it necessary to substitute non-heavy metal inhibitors (organics) for those used in the past. Often the transition requires control changes as well as a change in chemical treatment. Whereas the heavy metal programs performed well near neutral pH and required few additional biocides, the new programs require stable operating conditions at a higher pH, which means the addition of a scale inhibitor or dispersant, as well as a biocide for bacterial control.

Because the modern programs depend heavily on good control, it is necessary to monitor the process conditions of importance and monitor the performance of the chemical additives in the system on a frequent, if not continuous, basis.

Most cooling water systems have a general operating envelope within which the system must operate. This is usually determined by a combination of factors such as the quality and quantity of source water available, the cost of water disposal, the heat load, and others. A program of corrosion control (in combination with a scale control program) is set up based on operational targets of total dissolved solids content, pH, recirculation rate, etc. This means that both operational variables and the corrosion rates need to be monitored.

What Should a Corrosion Control and Monitoring Program Contain?

In order to effectively put together a corrosion control program, the specific corrosion problem or problems involved must be identified by the type of corrosion (general or localized) and the causes, if known. Once the symptoms and problems have been identified, it will be possible to select a method of control and a method of monitoring the various parameters to confirm that corrosion is under control, Analysis of the data by operations personnel is also a necessary part of any program. These data must be used to help maintain expected corrosion rates over a long period of time.