

Corrosion basics



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INTRODUCTION

Based on a recent survey conducted by the National Association of Corrosion Engineers of USA, expenditures for corrosion control have almost doubled since 1975 from an estimated \$9 billion to nearly \$17.7 billion annually. And, based on industry growth, these figures will continue to grow rapidly over the next few years.

As consultants in industrial water treatment technology, it is our responsibility to be thoroughly knowledgeable in specific water treatment topics such as corrosion control.

Therefore, this section will be entirely devoted to the study of corrosion and the various methods used to control it in industrial cooling water systems.

CORROSION REACTIONS

It has been demonstrated that potential differences within a metal, or between two metals, will cause chemical reactions at the anode and cathode. Anodic reactions are typified by the dissolution of iron:



Analogous reactions occur in other metals. The electrons migrate through the metal to the cathode area where they react in any one of several ways.

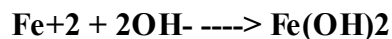
Some typical cathodic reactions are as follows:

- a. Hydrogen ion reduction $2\text{H}^{+} + 2\text{e}^{-} \rightarrow \text{H}_2$ Important in acidic solutions.
- b. Reduction of water $2\text{H}_2\text{O} + 2\text{e}^{-} \rightarrow \text{H}_2 + 2\text{OH}^{-}$ Occurs normally in natural waters.
- c. Oxygen reduction $\text{O}_2 + 4\text{H}^{+} + 4\text{e}^{-} \rightarrow 2\text{H}_2\text{O}$ Occurs in aerated acidic solutions.
- d. Oxygen reduction of water $\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^{-} \rightarrow 4\text{OH}^{-}$ Important in natural, aerated waters.
- e. Ferric ion reduction $\text{Fe}^{3+} + \text{e}^{-} \rightarrow \text{Fe}^{2+}$ Occurs under acidic, turbulent conditions (e.g. acid cleaning).
- f. Sulfate ion reduction $4\text{H}^{+} + \text{SO}_4^{2-} \rightarrow \text{S} + 2\text{H}_2\text{O}$ Occurs in the presence of sulfate reducing bacteria.
- g. Metal ion reduction (plating) $\text{M}^{n+} + \text{ne}^{-} \rightarrow \text{M}$ Involves more noble metals in solution. The most frequent cathodic reactions are a, b, c and d.

Negatively charged ions, such as hydroxyl ions produced at the cathode, migrate to the anode of the corrosion cell. Positively charged ions will move toward the cathode.

This movement of ions can cause additional reactions at the anode.

Hydroxyl ions will combine with the ferrous cations produced by dissolution of the metal:



The ferrous hydroxide produced has a very low solubility and is quickly precipitated as a white floe at the metal-water interface. The floe is then rapidly oxidized to ferric hydroxide:



Dehydrolysis of this product leads to the formation of the corrosion products normally seen on ferrous surfaces, red dust and hydrated ferric oxide:



As solid corrosion products are precipitated at the anode, they may cause the precipitation of other ions from the water. Thus, a corrosion film may show traces of hardness salts, or suspended matter like mud, sand, silt, clay or microbiological slime.

The structure of the entire surface film, including corrosion products and inclusions, is a major factor in determining the total amount of corrosion which will take place. If a porous film forms over the metal, corrosion can continue, because metal ions can penetrate it and reach the solution interface. If, however, a tight, adherent film is formed, ionic diffusion is prevented and the metal will no longer dissolve.

Most corrosion occurs at the beginning of a metal's service life. Initially, metal dissolution is not impeded by a film of corrosion products. In time, the film will retard, or halt the corrosion. The degree to which such a film can impede corrosion is a complex function of the corrosion reactions, the structure of the deposit and the water velocity.



CORROSION THEORY

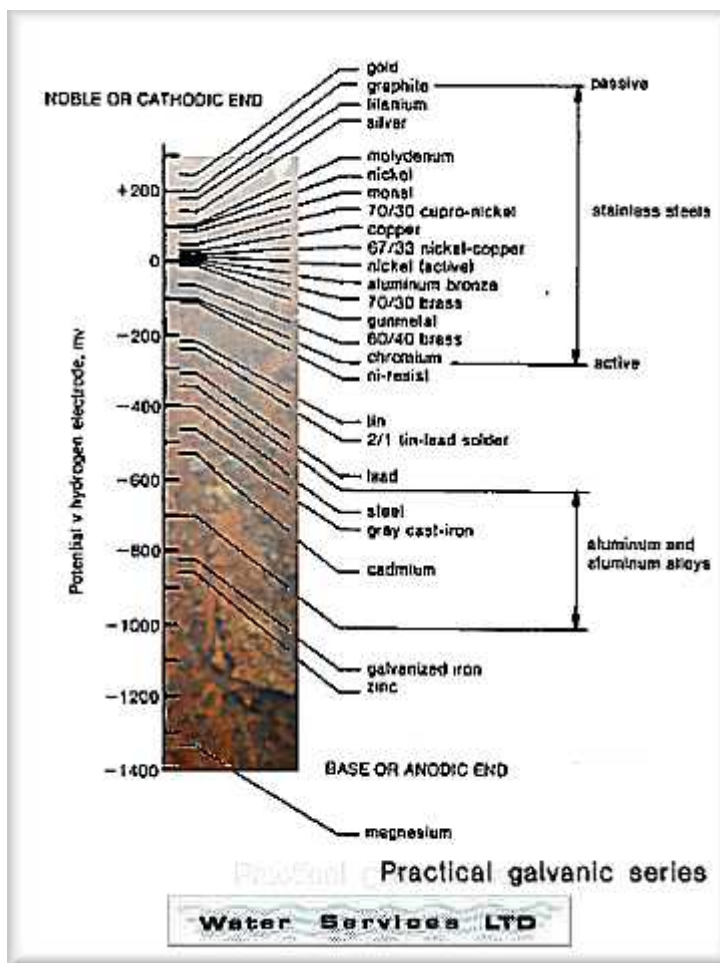
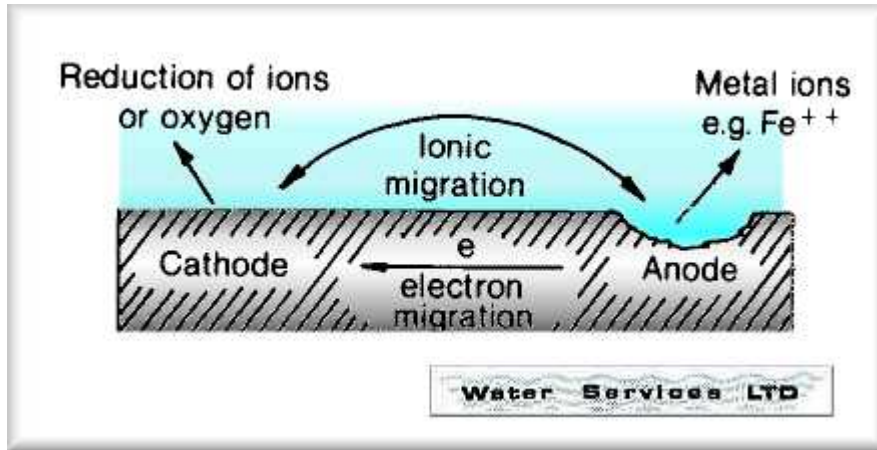
The search for a better understanding of the actual mechanism of corrosion has been actively pursued for over a hundred years. We understand what occurs during many corrosion processes, but the search is by no means complete; many areas remain unexplored or little understood.

However, our current knowledge of what takes place during the corrosion process has been sufficient to create effective tools to combat corrosion in most situations.

Corrosion is an electrochemical process in which a difference in electrical potential develops between two metals or between different parts of a single metal. This voltage can be measured when a metal is electrically connected to a standard electrode.

The electrical potential of a metal may be more or less than the standard, in which case the voltage is expressed as either "positive" or "negative". This difference in potential allows current to pass through the metal causing reactions at anodic and cathodic sites.

These sites constitute the corrosion cell, as shown in the figure below.



The anode is the region of lower potential. Conversely, the cathode is the region of higher potential. At the anode, metal ions go into solution. In general, the lower the potential of the anode, the greater the amount of metal dissolution and the more serious the corrosion problem.

The extent of the corrosion is also a function of the capability of ions and electrons to travel through the water phase and participate in chemical reactions. Waters high in dissolved solids are more conductive and cause

more severe corrosion problems. Thus, seawaters are generally more corrosive than surface supplies.

Any metal immersed in water will soon develop a measurable potential. Those of lower potential can be expected to corrode more easily and extensively than those of higher potential. Theoretically, we can, therefore, assume that if two metals are coupled, the one of lower potential would become the anode and actively corrode. The figure below shows the galvanic series developed for metals immersed in seawater. When two metals, as shown in the figure, are coupled, we would expect that the metal lower in the series would corrode.

It should be noted that the measured potentials shown in the illustration were developed under specific conditions of composition, temperature and velocity; and that in practical situations, the actual conditions may differ.

Anodic	Zinc Galvanized Aluminum Steel Brasses Copper Cu/Ni Alloys Nickel	Corrodes First
Cathodic	Stainless Steel	Protected

Practical galvanic series of metals and alloys

In an actual situation, if a pair of metals of different potential were coupled, problems within the system would probably exist. The result of coupling two metals of closer potential is more difficult to predict. Many other factors must be considered before

POLARIZATION

Polarization reduces the driving force of the corrosion reaction and minimizes metal loss by changing the potential of either the anode or the cathode, or both, so that the difference in potential between them is reduced to a minimum.

A basic concept of kinetics states that the rate of an overall reaction can be controlled by the rate of its slowest step; this applies to the corrosion reaction. Cathodic reactions are generally much slower than those occurring at the anode. Therefore, control of the overall corrosion rate can be accomplished by controlling the rate at the cathode and achieving polarization.

Control of the main cathode reactions, hydrogen or oxygen reduction, requires an understanding of their kinetics. Le Chateller's Principle states that a reaction can proceed to completion with an overabundance of reactants and/or removal of products. Applying this to the cathodic equations listed, it becomes clear that equations "a" and "b" will proceed if hydrogen gas is generated at the cathode; similarly, equations "c" and "d" will proceed if a sufficient supply of oxygen is available at the cathode.

Hydrogen will bubble off the cathode only when the cathode reaches a certain potential. The difference in potential between the cathode and a hydrogen electrode at equilibrium in the same solution is defined as hydrogen overvoltage. This overvoltage decreases with increasing temperature and surface roughness. The overvoltage needed for hydrogen evolution for some common metals is found in the table below.

Normally, the available hydrogen will be insufficient to exceed the overvoltage.

Metal	overvoltage in Volts
Platinum	0.12
Aluminum	0.19
Nickel	0.24
Iron	0.27
Silver	0.29
Copper Artificial Graphite Gold	0.33 0.35 0.36
Lead	0.42
Tin	0.49
Cadmium	0.50
Magnesium	0.59
Zinc	0.75

Cathode overvoltage of hydrogen on common metals

In waters of low pH, with relatively high concentrations of hydrogen ions, overvoltage is easily overcome. For this reason, equations "a" and "b" are the rate-controlling cathodic reactions. It also explains the rapid corrosion of iron and similar metals in acids

Some metals do not corrode in acid solution; these "noble" metals are more cathodic than hydrogen and will be reduced in preference to hydrogen ions. For example, copper does not corrode in an acid if there are no oxidizing agents present.

Because the evolution of hydrogen gas is part of the corrosion cell process, the cell will be polarized when the cathodic potential is reduced by a film of monatomic adsorbed hydrogen. This buildup of hydrogen, in turn, reduces the driving force of the overall corrosion reaction. Conversely, removal of hydrogen from the cathode surface will depolarize the corrosion reaction and lead to increased metal loss. At low pH, on metals less cathodic than hydrogen, the concentration of the latter can build to a point where overvoltage is overcome and hydrogen gas evolves.

In natural waters, where pH levels are far too high to overcome hydrogen overvoltage, the presence of dissolved oxygen usually controls the cathodic reaction rate. Equations "c" and "d" demonstrate the reactions involved. One logical corrosion control method, therefore, involves governing the amount of oxygen available to the cathode surface. Oxygen is brought to the metal by convection through the bulk of the cooling water and then by the diffusion through a thin laminar water film at the metal surface. If the amount of oxygen diffusion to the metal surface can be controlled, the corrosion reaction can be polarized. This is precisely the mechanism of cathodic corrosion inhibitors. They form an impervious film, which prevents the diffusion of oxygen to the cathode site. Another more costly way to remove oxygen involves mechanical deaeration techniques; these are often used in boiler operations but are usually uneconomical for most open cooling water systems. For ferrous-based materials, oxygen depolarization will be the determining factor in almost all cooling water situations, since pH is maintained at levels where hydrogen evolution effects are minimal.

It is relatively easy to protect closed systems. Any dissolved oxygen present is quickly used in the formation of oxide films along metal surfaces. Since the system is closed, no further oxygen is available. The pH of the system is kept fairly alkaline to maximize hydrogen overvoltage. Therefore, the main cathodic reactions are under control. Compare this to an open cooling water system where heat is rejected by evaporation to the atmosphere. In this situation, the water is constantly being resaturated with oxygen, which results in its subsequent availability to depolarize the corrosion cell. Open systems require more sophisticated corrosion inhibitor applications to maintain proper corrosion control.

ANODIC POLARIZATION

Anodic surfaces can be polarized by formation of a thin, impervious oxide layer. This film formation is accomplished by a mechanism known as chemisorption and is attributed to lower valence bonding at metal sites. Stainless steel naturally forms such films.

With most metals, however, the film formation must be aided by the addition of such anodic corrosion inhibitors as chromate, nitrite, etc. These and other anodic corrosion inhibitors will be discussed in more detail later in this section.

PASSIVITY

When corrosion reactions are completely polarized, the metal is said to be in a "passive state". At this point, there is no difference in potential between the anode and cathode areas, and corrosion ceases. When polarization is disrupted in a passive metal at a given point, a very active anodic site is set up, with resultant accelerated local corrosion, particularly if the metal was strongly anodically polarized.

CHEMICAL FACTORS

WATER COMPOSITION

The nature of the water phase, including dissolved and suspended matter, is integral to the subject of corrosion control. These aspects are discussed briefly to establish general guidelines. The exact constituents of the water phase are unique to any one water supply or application.

Therefore, the specific problems encountered in any plant' operations are, in a sense, similarly unique. Proper corrosion control requires that each case be considered separately. Often, the treatment program that works well for one plant may fail at a neighboring installation.

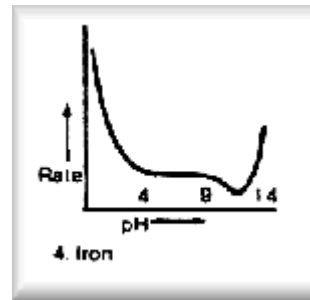
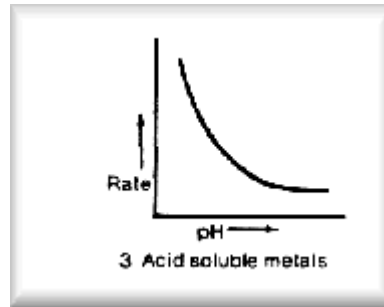
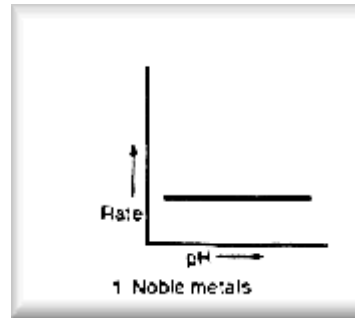
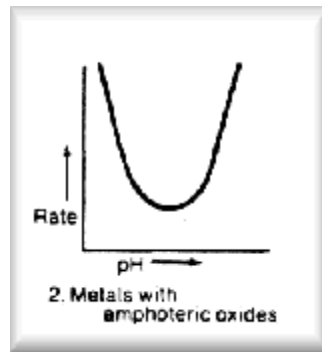
pH

Between pH 4.3 and 10.0 in natural, aerated waters at normal temperatures, changes in pH will affect the degree to which steel is corroded. In the case of ferrous-based materials, the solution just outside the anode is mildly alkaline since it is generally saturated with ferrous hydroxide.

However, below pH 4.3, where there is free mineral acidity in the water, corrosion progresses rapidly. In the pH range, overvoltage plays a more significant role in the corrosion process. Variations in the macrostructure of the metal or in the water interface become more important.

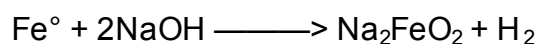
The actual effect of pH on a particular metal is determined by the behavior of its oxide. If the oxide is soluble in acidic media, the metal will corrode rapidly in this environment. If the oxide will readily dissolve in alkaline media, there will be extensive corrosion in that pH range. Most metals fall into the first category.

Occasionally, a metal oxide will dissolve in both acid and alkaline solutions; these metals are referred to as "amphoteric". The metal will have its greatest stability, from a corrosion standpoint, at some intermediate pH range. Aluminum and zinc are amphoteric. Their corrosion rates are minimal at pH 6.5 and 11.5, respectively. Some metal oxides are insoluble at any pH. Their corrosion rate will, therefore, be independent of pH. "Noble" metals, those at the top of the galvanic series, will behave in this way. The figure illustrates these points further.



Variation in corrosion rate with pH value

A number of odd trends are evident in the behavior of iron. As the pH increases to 4.0, the behavior is similar to that of an acid-soluble metal. Between pH 4.3 and 10.0, the corrosion rate is less influenced by pH, because oxygen depolarization is the principal factor determining corrosion. Any further pH increase reduces the corrosion rate, until a minimum value is attained at about pH 12. At this point, iron behaves amphotERICALLY; the corrosion rate again begins to rise with increasing pH. Interestingly enough, this results from hydrogen evolution; iron reacts with strong caustic solutions to liberate hydrogen and form the ferroate ion.



Thus, we see that hydrogen evolution controls corrosion of ferrous-based materials at both extremes of the pH scale.

DISSOLVED SALTS

The corrosion rate for metals associated with natural, low-solids water, at normal temperature, will accelerate as the concentration of the dissolved salts in the water increases. The corrosion rate may, thereafter, decrease in more heavily concentrated solutions, as a result of precipitation of dissolved salts as their solubility products are reached. In a dilute solution, increased electrical conductivity causes the corrosion rate to increase. For a concentrated solution, precipitation could quite possibly result in a barrier film, which would retard corrosion.

The ionic constituents in normal waters have various effects on the corrosion rate. For instance, the chloride ion, and to a lesser extent, the sulfate ion are

capable of penetrating passive films and setting up highly active, local anodic sites. Conversely, hardness ions and alkalinity have an inhibiting effect on corrosion; the precipitated products of various hardness salts often inhibit corrosion.

DISSOLVED GASES

A number of gases are normally found dissolved in water; these include carbon dioxide and oxygen. Other gases may also be present as a result of contamination or other control programs. Three typical examples of these are ammonia, hydrogen sulfide and chlorine.

Carbon Dioxide

The gradual solution of carbon dioxide into water will decrease pH by the formation of carbonic acid, which adds acidity to the water and thereby promotes hydrogen evolution.



Oxygen

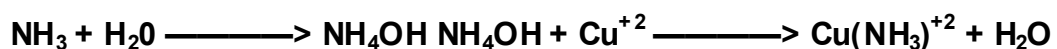
The amount of dissolved oxygen in water is directly related to its temperature, pressure, and surface area. Dissolved oxygen in the water acts as a cathodic depolarizer, promoting corrosion.

A special case of oxygen corrosion is mentioned briefly here and discussed in greater detail later in this section. When water has unequal oxygen concentrations, a differential aeration cell is set up. A very common manifestation of this is under-deposit corrosion.

Any porous deposit on a metal surface, whether from precipitated salts, suspended matter, or biological growth, will almost always have an oxygen-deficient environment underneath it. This leads to the formation of an active anodic site under the deposit and severe localized corrosion.

Ammonia

Ammonia is generally introduced into water as a result of process contamination. It will selectively corrode copper in the presence of oxidizing agents.



This soluble copper-ammonium complex is very corrosive to copper.

Hydrogen Sulfide

Hydrogen sulfide is one of the most harmful gases that can enter a cooling water system. It normally results from process contamination, especially in refineries and petrochemical plants, or is produced by the reduction of sulfate ions by sulfate-reducing bacteria.

The gas promotes active corrosion in two ways. Because it is acidic, it causes low pH attack. Secondly, it is responsible for the formation of iron sulfide, which is cathodic to iron and leads to galvanic corrosion.

Chlorine

Chlorine gas is the most commonly used toxicant for the control of microorganisms in cooling water systems. Upon entering the water, it hydrolyzes to form hypochlorous and hydrochloric acid. This action reduces the pH of the recirculating water and causes increased corrosion. On many metals it also retards formation of certain protective corrosion inhibitor films.

SUSPENDED MATTER

Mud, sand, silt, clay, dirt and other particles may enter a cooling water system either as airborne contamination or as part of the system's makeup water supply. In areas of the system where sedimentation of these materials take place, porous deposits are easily formed and differential aeration cells are quickly established, which can cause more corrosive damage than precipitated salts.

MICROORGANISMS

Microbiological growth often presents very special problems. Hydrogen is metabolized by many species, causing depolarization of the corrosion cell, similar to the action caused by dissolved oxygen. Anaerobic bacteria form differential aeration cells and accelerate local attack. Some species produce acidic compounds.

Desulfovibrio desulfuricans, a type of sulfate-reducing bacteria, produce hydrogen sulfide by reduction of the sulfate ions found in almost all water supplies. Such sulfate oxidizers as the *Thiobacillus* oxidize the sulfate ion to sulfuric acid and cause low pH attack.

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