



## Understanding Corrosion

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### Introduction

The purpose of this article is to present the basic principle and the most common forms of corrosion. Some general methods of control, prevention, and mitigation for each type of corrosion will be discussed but will not be covered in-depth.

### Basic corrosion principle

When a metal is exposed to certain environment and conditions, such as water (including moisture), chemicals (acid, caustic, salts), corrosive gases (O<sub>2</sub>, CO<sub>2</sub>) and/or high temperature, the metal will corrode. For a corrosion to take place, there must be both an *anodic* and a *cathodic* reaction. The anodic-cathodic reaction is a form of oxidation-reduction. The anodic reaction, which is the oxidation phase, takes place at the anodes of the metal. The cathodic reaction, or the reduction phase, takes place at the cathodes of the metal.

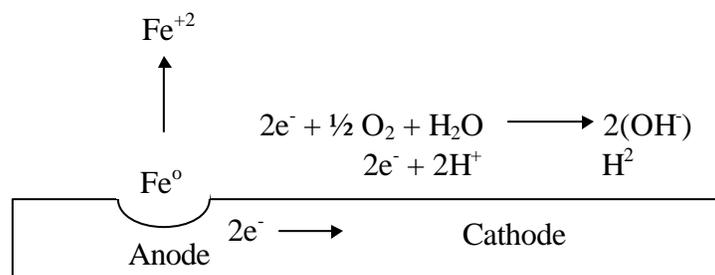
### What are anodes and cathodes?

Metals, such as iron, copper, and zinc, are formed by a myriad of processing such as melting, extrusion, casting, forming, heat treating, welding, galvanizing, cutting, rolling, and shaping. The processing leaves microscopic irregularities in structure and composition. The irregularities are even more pronounced in alloyed metals where different metals are combined. Impurities may also be added during processing. A metal, therefore, is not one single crystal but a mixture of crystals and grains that are randomly oriented. The boundaries between the crystals are weak and active. The sites where metals are shaped (i.e., cutting, bending) are subjected to stress. For corrosion purposes, the sites that are weak, active, and stressed are the anodes, while the cathodes are the noble, inactive, and unstressed areas.

### Electrochemical process

As indicated earlier, for corrosion to take place, there must be an anodic-cathodic (oxidation-reduction) reaction. In the anodic/oxidation stage, the metal is oxidized at the anode. Electrons are released by the oxidation. The oxidized metal is lost to the water solution. The free electrons travel through the metal to the cathode (like electricity travelling through wires) where they react with water, dissolved oxygen, and/or hydrogen ions, completing the cathodic/reduction stage. And since corrosion involves both electrical and chemical reactions, it is also referred to as an *electrochemical* process.

Here is a simple illustration:



The cathode acts as a receptor for the electrons. A larger cathodic area will draw more electrons from the anode, resulting in more metal loss at the anode. Therefore, the larger the cathodic area in relation to the anodic area, the larger the potential for corrosion, and vice versa. To illustrate, if you have a very small anodic area, and a huge cathodic area, all the metal loss will occur in the small anodic area to satisfy the electron demand by the cathode, resulting in a localized and/or pitting corrosion. Pitting corrosion looks like the metal has been drilled through, resulting in premature failure. Fig. 1 shows an example of pitting corrosion.



Figure 1 - Example of Pitting Corrosion

Conversely, if you have a large anodic area and a small cathodic area, given the same environment and conditions, corrosion rate will decrease, usually resulting in a general and uniform corrosion.

In the cathodic/reduction stage, the electrons react with oxygen and water at the cathode to form hydroxyl ions ( $\text{OH}^-$ ). They also react with hydrogen ion ( $\text{H}^+$ ) to form hydrogen gas ( $\text{H}_2$ ).

The hydroxyl ions and/or the hydrogen gas are formed at the cathodes. They act as barriers preventing the water, oxygen, hydrogen, and electrons from further converging and reacting. The barrier reduces the available cathodic sites, slowing down the electron transfer, and eventually slowing down the corrosion rate. This phenomenon is called **Polarization** of the cathodes.

As the cathode can be polarized, it can also be **depolarized**. These barriers can be stripped by high water turbulence/flow. If the water solution is acidic, as in the presence of dissolved  $\text{CO}_2$  ( $\text{CO}_2$  and water forms carbonic acid), the dissociated hydrogen ions will react with the hydroxyl ions to form water, stripping the hydroxyl ion barrier while introducing water again to the cathode. Dissolved Oxygen can also depolarize the cathode, by combining with the hydrogen at the cathode, destroying the hydrogen barrier, producing water at the cathode, resuming the cathodic/reduction process.

The anodic-cathodic corrosion can be controlled by disrupting the oxidation-reduction reactions described above, i.e., by reducing dissolved oxygen, increasing pH, inhibiting the anode/cathode, prevention of depolarization, and creating other forms of barrier, i.e., coatings.

### **Deposit and/or Crevice Corrosion**

Basically, when you have a deposit and/or a crevice on a metal surface, the concentration in the deposit/crevice will change over time and can be substantially different from the bulk water or environment.

In the case of dissolved oxygen (DO), it gets depleted in the deposit/crevice over time while it remains higher outside the deposit/crevice, resulting in an **oxygen differential cell**. The area in the deposit/crevice becomes anodic to the outside area, accelerating corrosion in the deposit/crevice. The bigger the difference in DO between the deposit/crevice and the bulk environment, the higher the corrosion potential.

The deposit/crevice also acts like a trap allowing corrosive elements like chlorides and sulfate to enter but not to leave, similar to a greenhouse effect. Over time, these corrosive elements build up, creating a **concentration cell**, corroding the surface in the deposit/crevice.

Another type of deposit is caused by **tuberculation**. Remember when the metal is oxidized and lost at the anode? This metal will react with available oxygen and alkalinity to form iron oxide and iron hydroxide, both of which are insoluble voluminous solids. They can settle and deposit on the metal forming a mound. This is like digging ground and dumping the dirt back. Like other deposits, tuberculation will cause concentration cell corrosion. Tuberculation can also slough off and plug other critical areas. Large tuberculation can reduce pipe diameter, increasing water flow resistance, and other related problems. Fig 2 is an example of tuberculation.



Figure 2 - Example of Tuberculation

Certain microorganisms can also thrive in a deposit/crevice which can lead to **microbio induced corrosion (MIC)**. These bacteria produce acid metabolites as part of their metabolism. Some bacteria produce slime which can attract deposits, causing differential cell corrosion. Iron depositing bacteria cause oxidation and subsequent deposition of tuberculation.

Corrosion inhibitor is usually employed to control corrosion, but it cannot penetrate the deposits/crevices leaving these areas unprotected and vulnerable to corrosion. The mode of corrosion control here is to prevent the settling of any deposit via chemical dispersion, purging, and filtration. A good microbio program must also be employed to control any microorganism activity.

## Galvanic Corrosion

Galvanic corrosion lies in the principle that all metals have a galvanic potential which is a ranking of corrosion potential. As you have learned, all metals will corrode by themselves. But when 2 dissimilar (different) metals are connected, irrespective of the type of metals, one of the metals becomes anodic to the other, and will corrode faster than it would by itself. Incredibly, the corrosion on the cathodic metal slows down or can even stop altogether.

Table 1, condensed from the MIL-STD-889, shows a partial list of metals and their galvanic ranking. The metals toward the top of the list are anodic to the metals toward the bottom. The farther apart they are in the table, the greater the galvanic difference, the greater the expected corrosion on the anodic metal. The driving force for corrosion is the potential difference between the 2 metals.

The principle of anodic-cathodic relativity also applies here. The larger the cathodic metal relative to the anodic metal, the greater, deeper, and more severe the corrosion potential would be, and vice versa.

As you've also learned, for corrosion to take place, the electrons must travel from the anode to the cathode. If you can stop this electron flow, you will stop the anodic-cathodic reaction. In a dissimilar metal connection, a dielectric union can be installed between the 2 metals, insulating the flow of electrons, to effectively stop the galvanic corrosion.

Using this concept, a steel metal can be protected by attaching it to a magnesium metal, or by coating it with zinc. The magnesium or zinc becomes the anode, corroding preferentially over the steel, thus sacrificing the magnesium or zinc to protect the steel from corrosion.

Knowing the galvanic ranking allows an engineer to choose the proper combination of metals and surfaces to minimize corrosion potential, and ultimately minimizing structural failures.

### Dissolved Gases

Dissolved gases such as oxygen, carbon dioxide, ammonia, sulfur can all contribute to corrosion, by direct oxidation, depolarization, and chelation.

To reduce their impact on corrosion, you may consider reducing these gases via mechanical pre-treatment methods such as deaeration, and chemical methods such as oxygen scavengers.

### Temperature

Higher temperature increases chemical reaction rate. And since corrosion is an electrochemical reaction, an increase in temperature will increase corrosion rate. Generally, for every 30°F increase in temperature, corrosivity doubles. In an open system, where the dissolved oxygen (DO) is allowed to escape at higher temperature, corrosion peaks at about 150°F and then drops off as the DO drops. In a closed system, where the DO is trapped, corrosivity continues to increase with temperature.

### Filiform Corrosion

This type of corrosion occurs under a protective film such as painting or other coatings that has been breached, allowing corrosive elements to permeate through. The characteristics of this corrosion are very similar to the deposit/crevice corrosion. Filiform corrosion is occasionally seen on water condenser tube sheets that have been coated with epoxy.

It can be minimized by preparing the subsurface properly prior to coating and by choosing the right coating material with the proper adhesion strength for the application.

Table 1 – Galvanic Series  
(condensed from MIL-STD-889 listing)

Anodic – metals toward the top
Magnesium
Zinc
Beryllium
Aluminum
Cadmium
Uranium
Lead
Steel
Iron
Tungsten
Brass
Bronze
Copper
Copper-nickel
Admiralty brass
Stainless steel 304 (passive)
Stainless steel 316L (passive)
Titanium
Silver
Gold
Graphite
Cathodic – metals toward the bottom



Fig 3 - Example of Filiform Corrosion

**Mechanically Induced Failure**

There are other types of metal failure that are mechanically induced, such as erosion, impingement, cavitation, stress caused by metalworking such as bending, stretching, rolling, shaping, and fatigue caused by repeated stress. In turn, they can cause or accelerate corrosion at the stress points. High stress areas are very active and are at a higher energy state. As such, these areas become anodic to the low stress areas. For example, the stress points on a boiler tube are at the ends where they are rolled onto the tube sheets. It is not uncommon to experience premature failures around these rolls. Such failure should not be blamed entirely on the corrosion inhibition program, unless all the tubes are corroding away.

**Summary**

Corrosion is nature's way of returning metal to its original natural ore state. It does so in various ways that are insidious, microscopic, and dynamic. It occurs in microenvironment which can be significantly different from the bulk environment, so any incipient corrosion usually does not manifest itself until it has become notably large. It is near impossible to predict corrosion accurately and more so to stop it completely. But we can slow it down with constant vigilant control and monitoring. We can even slow it down to glacier speed. But in the end, nature will still win. We can only delay the inevitable.