

# Understanding corrosion

A full primer on corrosion from basic principles and common forms, to methods of control and prevention.

By Mario C. Uy

**W**hen a metal is exposed to a certain environment or conditions such as water (including moisture), chemicals (acid, caustic, salts), corrosive gases ( $O_2$ ,  $CO_2$ ) and/or high temperature, the metal will corrode.

For 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.

## Anodes and cathodes

Metals, including 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.

These 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 (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 and the oxidized metal is lost to the water solution. The free electrons travel

through the metal to the cathode where they react with water, dissolved oxygen and/or hydrogen ions, completing the cathodic/reduction stage.

Since corrosion involves both electrical and chemical reactions, it is also referred to as an electrochemical process.

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 is in relation to the anodic area, the larger the potential for corrosion and vice versa.



## Mechanically induced metal 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.

—M.U.

## Pitting corrosion

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.



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 (OH<sup>-</sup>) and react with hydrogen ions (H<sup>+</sup>) to form hydrogen gas (H<sub>2</sub>).

The hydroxyl ions and/or the hydrogen gas are formed at the cathodes and 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 — a phenomenon called polarization of the cathodes.

### Cathode depolarization

While 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 CO<sub>2</sub> (CO<sub>2</sub> 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 and resuming the cathodic/reduction process.

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

### Deposit/crevice corrosion

When there is a deposit and/or a crevice on a metal surface, the con-

centration in the deposit/crevice will change over time and can be substantially different from the bulk water or environment.

Dissolved oxygen (DO), for instance, depletes 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 by 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 and corroding the surface in the deposit/crevice.

### Tuberculation

Another type of deposit is caused by tuberculation. When the metal is oxidized and lost at the anode, it will react with available oxygen and alkalinity to form iron oxide and iron hydroxide, both of which are insoluble voluminous solids.

These solids can settle and deposit on the metal, forming a mound.

**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*



*Plugging caused by tuberculation.*

Like other deposits, tuberculation will cause concentration cell corrosion and it can also slough off and plug other critical areas. Large tuberculation can reduce pipe diameter, increasing water flow resistance and causing other related problems.

### Microbio-induced corrosion

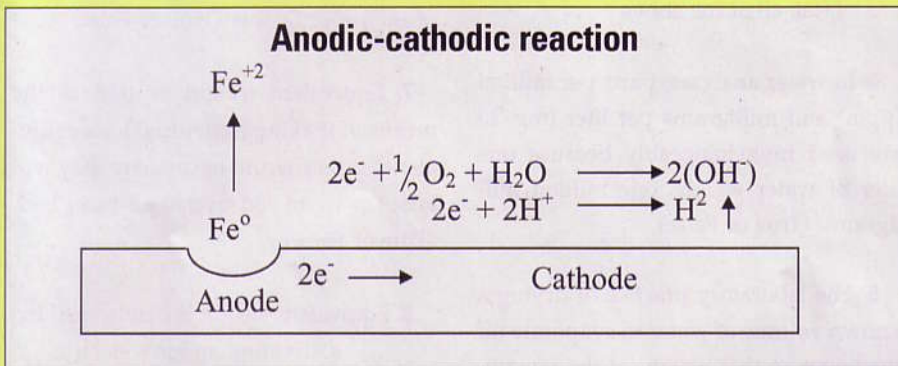
Certain microorganisms can also thrive in a deposit/crevice, which can lead to microbio-induced corrosion (MIC). These bacteria produce acid metabolites as part of their metabolism.

*(Concluded on page 83)*



(Continued from page 81)

Some bacteria produce slime that can attract deposits and cause 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, thereby leaving those 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 microbi 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 that is a ranking of corrosion potential.

While all metals will corrode by themselves, when two 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 (see page 81), 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 further apart the metals are in the table, the greater the galvanic difference and the greater the expected corrosion on the anodic metal. The driving force for corrosion is the potential difference between the two metals.

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

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 two 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.

### Dissolved gases

Dissolved gases such as oxygen, carbon dioxide, ammonia and 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 pretreatment 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 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 paint, allowing corrosive elements to permeate through. The characteristics of this corrosion are very similar to deposit/crevice corrosion.

Filiform corrosion is occasionally seen on water condenser tube sheets that have been coated with epoxy.

This corrosion 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. □

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