Corrosion Protection Principles

Or

Everything Your Mother Should Have Taught You about Corrosion

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Introduction

Corrosion of metals costs the world economy around US\$2.5 trillion per year, using up about 3.4% of global economic output (numbers from 2013; see http://impact.nace.org/ economic-impact.aspx). It is important for you as an engineer to understand its causes and how it can be prevented or slowed. This document summarizes those principles. I encourage you to seek additional information from reliable sources.

Causes of Corrosion

Corrosion happens when oxygen or a similar oxidizing chemical reacts with the metal, forming an inorganic compound, typically an oxide. This is the thermodynamically preferred (lowest energy) state of most metals when exposed to the environment. Notice when we dig metal ores out of the ground, they are generally not pure and energy must be used to process them into pure metals. So, keeping metals from corroding is your battle against the universe. I wish you success.

For many metals, the oxide crust or coating that forms on the outside of the metal becomes a protective barrier that reduces further corrosion by slowing the transport of oxygen to the native metal surface. This is known as "passivating" the metal. However, if that oxide coating has holes in it or it flakes off or crumbles, then it cannot protect the metal and corrosion will continue, eventually destroying the structural integrity of the metal component.

As an example, placing plain carbon steel in a humid environment can accelerate corrosion because the most common oxide is red Fe₂O₃, which is easily hydrated, causing it to expand. The expanded oxide develops gaps and flakes off the surface. In other words, water weakens the oxide coating and corrosion continues. The addition of acid and chloride, among other compounds, to the water weakens the oxide even further and rusting accelerates. On the other hand, alkaline solutions promote a more durable form of iron oxide, black Fe₃O₄, and so steel holds up quite well in alkaline solutions and tends to corrode much less.

High temperatures increase the rate of oxidation reactions as they do all reactions. Therefore, high-temperature oxidizing environments such as combustion reactors present a tough corrosion problem. So-called super alloys containing nickel or "refractory" metals like molybdenum or tungsten are often used in such environments.

Noble metals like gold and platinum are corrosion resistant because they do not readily react with oxygen. This can be observed by looking at a table of standard reduction potentials of the various elements where gold and platinum have potentials equal to or more positive than oxygen. Therefore, they do not form or need a protective oxide. So, if you wanted to make a durable set of religious records to pass on to future generations, gold would be a good choice of material.

Metals like aluminum and chromium readily react with oxygen but form a tough and impermeable oxide coating. Thus, they tend to corrode less than iron, especially in humid environments. The alloying of chromium with iron in order to make stainless steel works because of the durable chromium oxide coating that is formed on the mostly iron surface. Copper is like aluminum: its oxide holds up well to water at neutral pH, but it can be readily corroded in acidic solutions.

Protection Strategies

Based on the above causes, there are four main strategies for slowing or preventing corrosion. Keep in mind that corrosion could take place on any metal surface, such as inside a pipe and outside a pipe. These strategies can be used in combination, as applicable. Use them and make your mother proud.

Strategy 1. Change the chemical environment.

Some chemical environments are aggressively corrosive, and nothing can be done. On the other hand, if oxygen, water, or salt can be removed from the environment, pH can be adjusted, or temperature can be lowered, this can decrease corrosion.

In some closed-loop systems, such as a building heating/cooling system based on circulating water, use of "inhibitor" additives in the water can reduce corrosion by forming protective and self-repairing films on metal surfaces by adsorption of amine-based molecules and various anions.

Strategy 2. Change the structural material.

Choose a more corrosion-resistant metal, such as stainless steel or nickel-containing superalloy that forms its own durable oxide. These options are not cheap. Or, if appropriate, replace the metal component with polymer, ceramic, glass, or composite not subject to corrosion. Of course, non-metallic materials are subject to failure due to alternative degradation mechanisms, which must be considered.

Strategy 3. Add a coating.

Put a coating of polymer or ceramic on the metal to slow the rate of oxygen transport to the surface or prevent contact with water or other corrosion accelerators. For instance, painting the outside of metal surfaces is generally a lowcost solution. Using replaceable plastic linings inside tanks and pipes is another common strategy.

One downside to this is that the coating is not self-healing in the same way that the native metal oxide can be. This means if the polymer coating or paint is damaged or cracks off somewhere, corrosion can happen quickly. Even worse is if the corrosive solution gets in between the coating and the metal, leading to unobserved corrosion. Therefore, regular inspection, maintenance, and replacement is required. For instance, the Golden Gate Bridge in San Francisco has been continuously repainted since its completion in 1937. If you want a job for life, join that painting crew!

Strategy 4. Use cathodic or active protection.

This is based on the idea that sooner or later oxygen is going to get to the surface of the metal and attack it. If one "feeds the beast" by delivering electrons to the oxygen, then the metal will not be oxidized by the oxygen. The question is how to get these electrons to the metal to be protected—they must come from somewhere. There are two options:

Option A - sacrificial anode. Place the metal in direct contact with a more reactive metal. The more reactive metal (lower reduction potential) will preferentially corrode and will deliver its electrons to the more noble metal. The corroding metal is known as a sacrificial anode. It will corrode even faster than it would otherwise because it is "feeding the beast" for itself and for the protected metal. Isn't that charitable of it? Galvanized steel, which is steel with a thin coating of zinc, is commonly used for structural components including sheet metal, screws, and bolts. This coating must necessarily corrode in order to protect the steel. Similarly, a magnesium rod is placed inside of residential water heaters as a sacrificial anode. It is intended to be replaced every 6 years, though everyone forgets to do this and ends up having to eventually replace the entire water heater instead.

Option B - impressed current. Connect the metal to be cathodically protected to a DC power supply which is also connected to a counter electrode or anode. The anode could be another piece of metal, dense graphite, or a mixed metal oxide (MMO). The anode carries out an oxidation reaction that generates electrons. The power supply drives the electrons from the anode to the protected metal cathode.

For this method to work, there must also be ionic contact between electrodes, to provide a complete electrical circuit or loop for current to travel. This means the two electrodes must be immersed in the same ion-containing solution. This could be fresh water or seawater (each containing dissolved minerals), soil or concrete (with water and minerals in the pore spaces).

The amount of voltage—and therefore current—that is applied by the power supply must be tuned. Too little voltage/current will not adequately protect the metal. Too much voltage/current can cause the protected metal to have such an abundance of

electrons that it also generates hydrogen gas. Over a long time period the hydrogen can go into the metal lattice and cause embrittlement. Too much voltage/current also leads to unnecessary economic cost. The proper amount of voltage to be provided by the power supply depends on the configuration of electrodes and the chemical environment, but 1.0 volt is a good starting point for small systems (for large systems you may need to crank the voltage much higher).

Active electrical protection with impressed current can be a very reliable strategy, but it does require maintenance and the expense of continuous electrical power. It is used to protect large and valuable structures like buried pipelines and tanks. Very long or large structures will need to be surrounded by multiple evenly spaced anodes to provide uniform protection from oxygen attack.

Strategy 0. No protection at all.

Lastly, you should consider the strategy of doing nothing. Namely, there are occasional situations where the most *economical* solution to corrosion is to let it occur at its natural pace, and plan on using a low-cost pipe, valve, or structure with more frequent inspection and replacement.

Can Corrosion Ever Be Good?

There are a couple helpful uses of corrosion. The figure below shows a disposable heat pack (left) used to keep your fingers warm inside your gloves in the winter. The porous satchel contains powdered iron, salt, and carbon. Once it is removed from a sealed package, the oxygen and moisture from the air starts the iron corroding. Moisture from your body speeds this up. This reaction generates significant heat. In fact, you could say

that corrosion is just combustion in slow motion. The carbon is used to distribute the heat and moderate the reaction.

The figure also shows a smaller pack (right) that works on a similar principle, except that it is intended as an oxygen absorber. The powdered iron reacts with and scavenges oxygen. The pack is placed inside sealed packaging alongside food to be preserved for long term storage, such as dehydrated meat or fruit. Lack of oxygen will prevent bacteria and mold from growing.

