

Fundamentals of Corrosion and Corrosion Control for Civil and Structural Engineers

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Corrosion of a Coated Handrail

Corroded Rain Gutter

Corrosion on the Nose of the Statue of Liberty

Introduction

Corrosion can be defined as the degradation of a material due to a reaction with its environment.

Degradation implies deterioration of physical properties of the material. This can be a weakening of the material due to a loss of cross-sectional area, it can be the shattering of a metal due to hydrogen embrittlement, or it can be the cracking of a polymer due to sunlight exposure.

Materials can be metals, polymers (plastics, rubbers, etc.), ceramics (concrete, brick, etc.) or composites-mechanical mixtures of two or more materials with different properties. Because metals are the most used type of structural materials most of this paper will be devoted to the corrosion of metals.

Most corrosion of metals is electrochemical in nature.

Electrochemistry Fundamentals

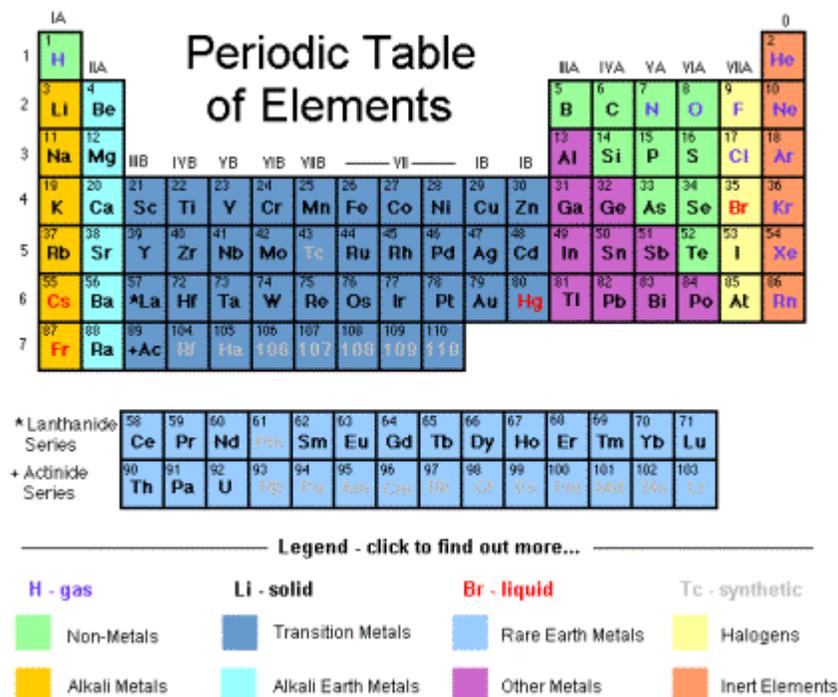
Atoms:

All matter is made of atoms composed of protons, neutrons, and electrons. The center, or nucleus, of the atom is composed of positively charged protons and neutral neutrons. The outside of the atom has negatively charged electrons in various orbits. This is shown schematically in the picture to the right where the electrons are shown orbiting the center, or nucleus, of the atom in much the same way that the planets orbit the sun in our solar system.

All atoms have the same number of protons (positively charged) and electrons (negatively charged). Therefore all atoms have a neutral charge (the positive and negative charges cancel each other). Most atoms have approximately the same number of neutrons as they do protons or electrons, although this is not necessary, and the number of neutrons does not affect the identity of the element.

The number of protons (atomic number) in an atom determines which kind of atom we have, and the atomic mass (weight) of the atom is determined by the number of protons and neutrons in the nucleus (the electrons are so small as to be almost weightless).

There are over 100 different elements that have been discovered. These are shown in the Periodic Table of the Elements below. The letter symbols for the elements come from their Latin names, so for example, H stands for hydrogen, C for Carbon, O for oxygen, while Fe stands for iron and Cu stands for copper.



Only a few of the elements are common, and most corrosion occurs due to only a dozen or so metallic elements (iron, aluminum, copper, zinc, etc.) reacting with common nonmetallic elements (oxygen, chlorine, sulfur, etc.).

Ions:

Ions are formed when atoms, or groups of atoms, lose or gain electrons.

Metals lose some of their electrons to form positively charged ions, e.g. Fe^{+2} , Al^{+3} , Cu^{+2} , etc.

Nonmetals gain electrons and form negatively charged ions, e.g. Cl^- , O^{-2} , S^{-2} , etc.

Molecules:

Compounds are groups of metals and nonmetals that form distinct chemicals. Most of us are familiar with the formula H_2O , which indicates that each water molecule is made of two hydrogen atoms and one oxygen atom. Many molecules are formed by sharing electrons between adjacent atoms. A water molecule has adjacent hydrogen and oxygen atoms sharing some of their electrons.

Acids and bases:

Water is the most common chemical on the face of the earth. It is made of three different constituents, hydrogen ions, hydroxide ions, and covalently bonded (shared electron) water molecules. Most of water is composed of water molecules, but it also has low concentrations of H^+ ions and OH^- ions.

Neutral water has an equal number of H^+ ions and OH^- ions. When water has an excess of H^+ ions, we call the resultant liquid an acid. If water has more OH^- ions, then we call it a base.

The strength of an acid or a base is measured on the pH scale. pH is defined by the following equation:

$$\text{pH} = -\log [\text{H}^+]$$

A detailed explanation of pH and acids and bases is beyond the scope of this paper. It is sufficient to note that some metals (e.g. zinc and aluminum) will corrode at faster rates in acids or bases than in neutral environments. Other metals, e.g. steel, will corrode at relatively high rates in acids but have lower corrosion rates in most neutral and basic environments.

Even a strong acid, with a pH of 0, will be less than 1/1000th by weight hydrogen ions. Neutral water, at a pH of 7, is less than 1 part H^+ in 10 million parts covalently bonded water molecules.

Mnemonic device: Many people have a hard time remembering whether an acid or a base has a high pH number. Just remember that acid comes before base in the alphabet and that low numbers come before high numbers. Acids have low numbers (less than 7), bases have high numbers (greater than 7). Neutral waters have pH's near 7 and tend to be relatively noncorrosive to many materials.

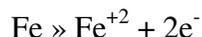
Electrochemical Cells

Oxidation and Reduction:

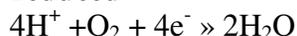
Metals are elements that tend to lose electrons when they are involved in chemical reactions, and nonmetals are those elements that tend to gain electrons.

Sometimes these elements form ions, charged elements or groups of elements. Metallic ions, because they are formed from atoms that have lost electrons, are positively charged (the nucleus is unchanged). When an atom or ion loses electrons it is said to have been **oxidized**.

A common oxidation reaction in corrosion is the oxidation of neutral iron atoms to positively charged iron ions:



The electrons lost from a metal must go somewhere, and they usually end up on a nonmetallic atom forming a negatively charged nonmetallic ion. Because the charge of these ions has become smaller (more negative charges) the ion or atom which has gained the electron(s) is said to have been **reduced**.



or

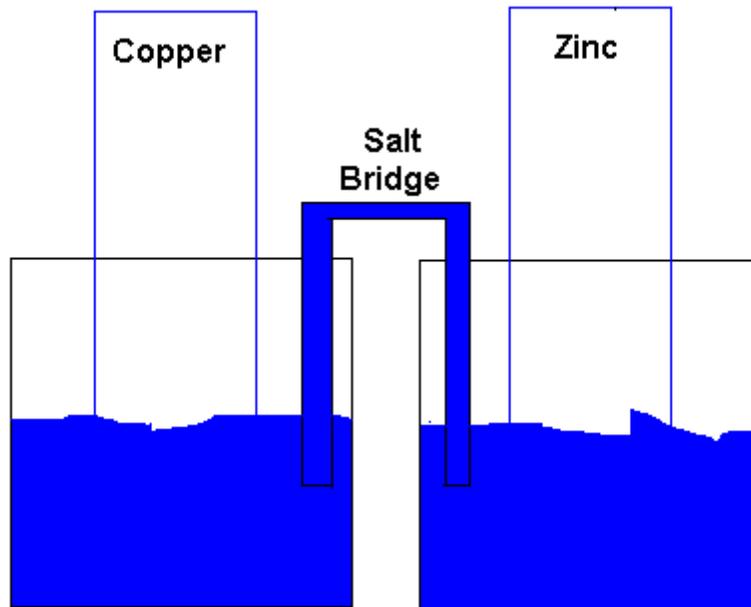


While other reduction reactions are possible, the reduction of oxygen is involved in well over 90% of all corrosion reactions. Thus the amount of oxygen present in an environment, and its ability to absorb electrons, is an important factor in determining the amount of oxidation, or corrosion, of metal that occurs.

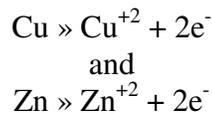
Mnemonic device: Many people have a hard time remembering what oxidation and reduction mean in terms of chemical reactions. If you just remember that reduction means “get smaller,” then you can remember that the electrical charge on a reduced chemical has gotten smaller (has more negative charges). The opposite reaction, oxidation, means that the charge has gotten larger (not so easy to remember).

Electrochemical Reactions:

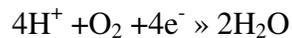
The two metal strips shown below are exposed to the same acid.



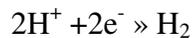
Both metals undergo similar oxidation reactions:



The electrons freed by the oxidation reactions are consumed by reduction reactions. On the copper the reduction reaction is:

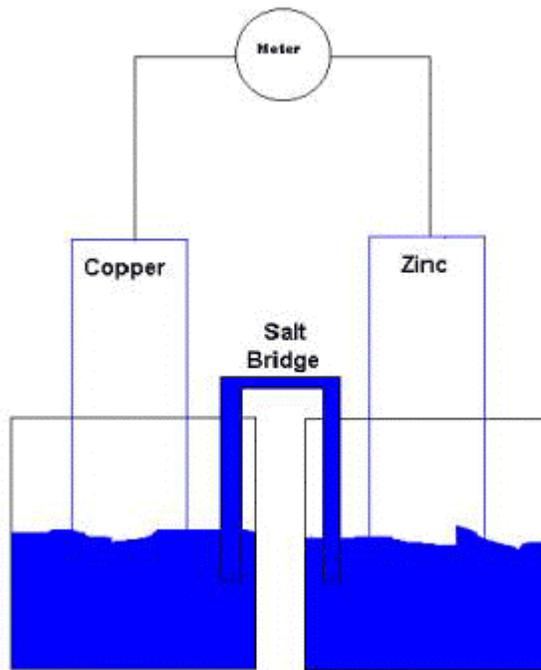


The corrosion rate of the copper is limited by the amount of dissolved oxygen in acid. On the zinc the reduction reaction is:



The hydrogen ions are converted to hydrogen gas molecules and can actually be seen bubbling off from the acid.

If we now connect the two metal samples with a wire and measure the electricity through the connecting wire, we find that one of the electrodes becomes different in potential than the other and that the corrosion rate of the copper decreases while the corrosion rate of the zinc increases. By connecting the two metals, we have made the copper a cathode in an electrochemical cell, and the zinc has become an anode. The accelerated corrosion of the zinc may be so much that all of the oxidation of the copper stops and it becomes protected from corrosion. This method of corrosion control is called cathodic protection.

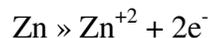


The reaction at the copper (cathode) becomes:

$$2\text{H}^+ + 2\text{e}^- \gg \text{H}_2$$

The voltage of the copper shifts to a point where hydrogen ion reduction can occur at the copper surface. The oxidation (corrosion) of the copper cathode may completely stop due to the electrical connection to the zinc anode.

The reaction at the zinc (anode) remains the same,



but the reaction rate increases due to the fact that the surface area of the clean (uncorroding) copper surface can now support a reduction reaction at a high rate.

Thus connecting these two metals virtually stopped the corrosion of the copper and increased the corrosion rate of the zinc. The zinc cathodically protected the copper from corrosion. Cathodic protection is a common means of corrosion control.

Mnemonic device: Anodes are those portions of an electrochemical cell that have mostly oxidation reactions. Cathodes are those locations of an electrochemical cell that have mostly reduction reactions. One way to remember which kind of reaction predominates at each kind of electrode is to note that anode comes before cathode in the alphabet just like oxidation comes before reduction. Anodes oxidize; cathodes reduce.

Why Metals Corrode

Metals corrode because we use them in environments where they are chemically unstable. Only copper and the precious metals (gold, silver, platinum, etc.) are found in nature in their metallic state. All other metals, to include iron-the metal most commonly used-are processed from minerals or ores into metals that are inherently unstable in their environments.



This golden statue in Bangkok, Thailand, is made of the only metal which is thermodynamically stable in room temperature air. All other metals are unstable and have a tendency to revert to their more stable mineral forms. Some metals form protective ceramic films (passive films) on their surfaces and these prevent, or slow down, their corrosion process. The woman in the picture below is wearing anodized titanium earrings. The thickness of the titanium oxide on the metal surface refracts the light and causes the rainbow colors on her earrings. Her husband is wearing stainless steel eyeglasses. The passive film that formed on his eyeglasses is only about a dozen atoms thick, but this passive film is so protective that his eyeglasses are protected from corrosion. We can prevent corrosion by using metals that form naturally protective passive films, but these alloys are usually expensive, so we have developed other means of corrosion control.



Galvanic Corrosion

Galvanic corrosion is an electrochemical action of two dissimilar metals in the presence of an electrolyte and an electron conductive path. It occurs when dissimilar metals are in contact.

It is recognizable by the presence of a buildup of corrosion at the joint between the dissimilar metals. For example, when aluminum alloys or magnesium alloys are in contact with steel (carbon steel or stainless steel), galvanic corrosion can occur and accelerate the corrosion of the aluminum or magnesium.

Galvanic Series In Sea Water

Noble

(least active)

Platinum

Gold

Graphite

Silver

18-8-3 Stainless steel, type 316 (passive)

18-8 Stainless steel, type 304 (passive)

Titanium

13 percent chromium stainless steel, type 410 (passive)

7NI-33Cu alloy

75NI-16Cr-7Fe alloy (passive)

Nickel (passive)

Silver solder

M-Bronze

G-Bronze

70-30 cupro-nickel

Silicon bronze

Copper

Red brass

Aluminum bronze

Admiralty brass

Yellow brass

76NI-16Cr-7Fe alloy (active)

Nickel (active)

Naval brass

Manganese bronze

Muntz metal

Tin

Lead

18-8-3 Stainless steel, type 316 (active)

18-8 Stainless steel, type 304 (active)

13 percent chromium stainless steel, type 410 (active)

Cast iron

Mild steel

Aluminum 2024

Cadmium

Alclad

Aluminum 6053

Galvanized steel

Zinc

Magnesium alloys

Magnesium

Anodic

(most active)

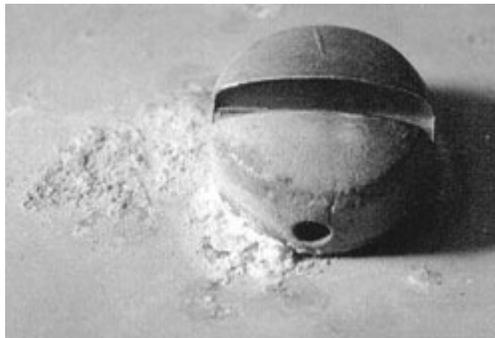
The natural differences in metal potentials produce galvanic differences, such as the galvanic series in seawater. If electrical contact is made between any two of these materials in the presence of an electrolyte, current must flow between them. The farther apart the metals are in the galvanic series, the greater the galvanic corrosion effect or rate will be. Metals or alloys at the upper end are noble while those at the lower end are active. The more active metal is the anode or the one that will corrode.

Control of galvanic corrosion is achieved by using metals closer to each other in the galvanic series or by electrically isolating metals from each other. Cathodic protection can also be used to control galvanic corrosion effects.



The scuba tank above suffered galvanic corrosion when the brass valve and the steel tank were wetted by condensation. Electrical isolation flanges like those shown on the right are used to prevent galvanic corrosion. Insulating gaskets, usually polymers, are inserted between the flanges, and insulating sleeves and washers isolate the bolted connections.

The photo below shows the corrosion caused by a stainless steel screw causing galvanic corrosion of aluminum. The picture shows the corrosion resulting from only six months exposure.



Uniform Corrosion

This is also called general corrosion. The surface effect produced by most direct chemical attacks (e.g., as by an acid) is a uniform etching of the metal. On a polished surface, this type of corrosion is first seen as a general dulling of the surface and, if allowed to continue, the surface becomes rough and possibly frosted in appearance. The discoloration or general dulling of metal created by its exposure to elevated temperatures is not to be considered as uniform etch corrosion. The use of chemical-resistant protective coatings or more resistant materials will control these problems.

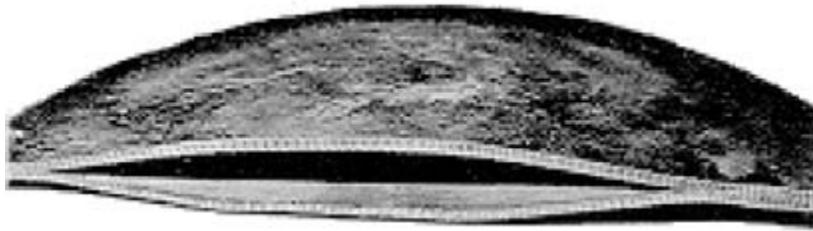
While this is the most common form of corrosion, it is generally of little engineering significance, because structures will normally become unsightly and attract maintenance long before they become structurally affected. The facilities shown in the picture below show how this corrosion can progress if control measures are not taken.



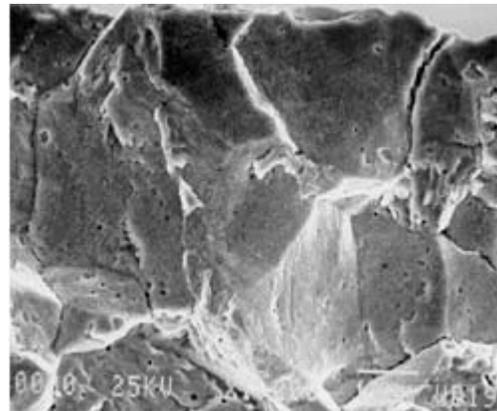
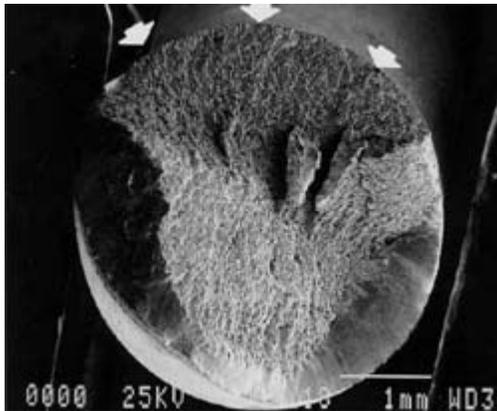
Hydrogen Damage

Hydrogen can cause a number of corrosion problems. Hydrogen embrittlement is a problem with high-strength steels, titanium, and some other metals. Control is by eliminating hydrogen from the environment or by the use of resistant alloys.

Hydrogen blistering can occur when hydrogen enters steel as a result of the reduction reaction on a metal cathode. Single-atom nascent hydrogen atoms then diffuse through the metal until they meet with another atom, usually at inclusions or defects in the metal. The resultant diatomic hydrogen molecules are then too big to migrate and become trapped. Eventually a gas blister builds up and may split the metal as shown in the picture below.



Hydrogen blistering is controlled by minimizing corrosion in acidic environments. It is not a problem in neutral or caustic environments or with high-quality steels that have low impurity and inclusion levels.



The broken spring above on the left was studied for failure analysis. Examination at high magnification in the scanning electron microscope (above right) reveals intergranular cleavage characteristic of hydrogen assisted cracking (hydrogen embrittlement). The part was zinc plated during refurbishment, and the hydrogen which entered the metal during the plating process had not been baked out. A postplating bakeout procedure should be standard for high strength steels.

Corrosion in Concrete



The picture on the left shows cracking and staining of a seawall. The pitting corrosion in the right photo occurred on an aluminum railing on a concrete causeway over an inlet to the Atlantic Ocean.

Concrete is a widely used structural material that is frequently reinforced with carbon steel reinforcing rods, post-tensioning cable or prestressing wires. The steel is necessary to maintain the strength of the structure, but it is subject to corrosion. The cracking associated with corrosion in concrete is a major concern in areas with marine environments and in areas which use deicing salts.

There are two theories on how corrosion in concrete occurs:

1. Salts and other chemicals enter the concrete and cause corrosion. Corrosion of the metal leads to expansive forces that cause cracking of the concrete structure.
2. Cracks in the concrete allow moisture and salts to reach the metal surface and cause corrosion.

Both possibilities have their advocates, and it is also possible that corrosion in concrete can occur either way. The mechanism isn't truly important, the corrosion leads to damage, and the damage must be controlled.

In new construction, corrosion in concrete is usually controlled by embedding the steel deep enough so that chemicals from the surface don't reach the steel (adequate depth of cover). Other controls include keeping the water/cement ratio below 0.4, having a high cement factor, proper detailing to prevent cracking and ponding, and the use of chemical admixtures. These methods are very effective, and most concrete structures, even in marine environments, do not corrode.

Unfortunately, some concrete structures do corrode. When this happens, remedial action can include repairing the cracked and spalled concrete, coating the surface to prevent further entry of corrosive chemicals into the structure, and cathodic protection, an electrical means of corrosion control.

Stress Corrosion Cracking

Stress corrosion cracking (SCC) is caused by the simultaneous effects of tensile stress and a specific corrosive environment. Stresses may be due to applied loads, residual stresses from the manufacturing process, or a combination of both.

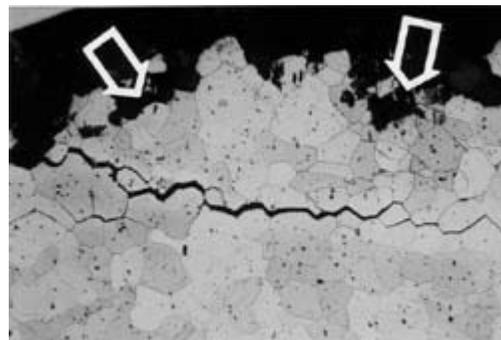
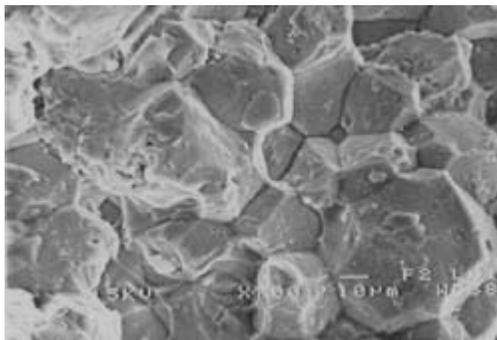


Cross sections of SCC frequently show branched cracks. This river branching pattern is unique to SCC and is used in failure analysis to identify when this form of corrosion has occurred.

The photo below shows SCC of an insulated stainless-steel condensate line. Water wetted the insulation and caused chlorides to leach from the insulation onto the hot metal surface. This is a common problem on steam and condensate lines. Control is by maintaining the jackets around the lines so that moisture doesn't enter the insulation or is quickly drained off.

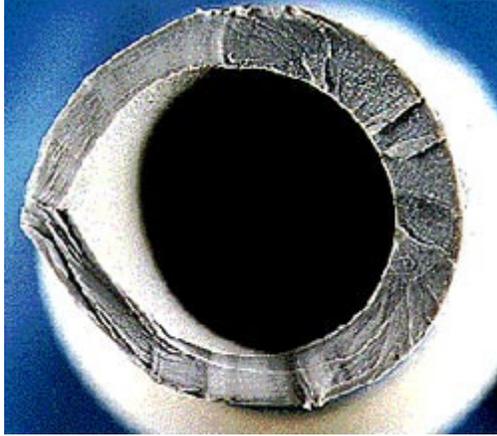


The next two photos show intergranular SCC of an aluminum aerospace part. The intergranular nature of the corrosion can be seen in the scanning electron microscope image on the left and in the microscopic cross section on the right. The arrows indicate the primary crack shown in both pictures. Note that secondary cracks are also apparent. These secondary cracks are common in stress corrosion cracking.



The failure above occurred on an aluminum alloy subjected to residual stresses and salt water.

Several years ago, wide spread use of plastic tubing was started in new house construction and for repair of old systems. Flexible tubing was used to connect faucets to the fixed metal piping. The picture below shows stress corrosion cracking after eight years in this service. The tubing was bent and stress cracks started at the outside tensile side of the tube. Flexible plastic piping is now used less often in this service-especially for hot water service.



Corrosion Control

There are a number of means of controlling corrosion. The choice of a means of corrosion control depends on economics, safety requirements, and a number of technical considerations.



Design



Engineering design is a complicated process that includes design for purpose, manufacturability, inspection, and maintenance. One of the considerations often overlooked in designing manufactured products is drainage. The corrosion of the automobile side panel above could have been minimized by providing drainage to allow any water and debris to fall off of the car instead of collecting and causing corrosion from the far side of the panel.

All of the other methods of corrosion control should be considered in the design process

Materials Selection

Carbon Steel

Most large metal structures are made from carbon steel-the world's most useful structural material. Carbon steel is inexpensive, readily available in a variety of forms, and can be machined, welded, and formed into many shapes.

A special form of carbon steel is known as weathering steel. Weathering steel does not need painting in many boldly exposed environments. Unfortunately, weathering steel has been misused in many circumstances where it could not drain and form a protective rust film. This has given the alloy a mixed reputation in the construction industry.

Where other means of corrosion control are not practical, other alloys can be substituted for carbon steel. This normally doubles or more the material cost for a

structure, and other corrosion control methods must be considered before deciding on the use of more expensive alternates to carbon steel.

Some forms of carbon steel are subject to special types of corrosion such as hydrogen embrittlement, etc. It is common practice to limit the allowable strength levels of carbon steel to avoid brittle behavior in environments where environmental cracking may occur. High strength bolts cannot be galvanized for the same reason-a concern that they may hydrogen embrittlement due to corrosion on the surface.

Protective coatings, cathodic protection, and corrosion inhibitors are all extensively used to prolong the life of carbon steel structures and to allow their use in environments where the environment would otherwise be too corrosive for their use.

Stainless Steels



The stainless steel body on this sports car is one example of how stainless steels can be used. The stainless steel is virtually immune to corrosion in this application-at least in comparison to the corrosion that would be experienced by conventional carbon steel or aluminum auto bodies.

Stainless steels are a common alternative to carbon steels. There are many kinds of stainless steels, but the most common austenitic stainless steels (300-series stainless steels) are based on the general formula of iron with approximately 18% chromium and 8% nickel. These austenitic stainless steels are frequently immune to general corrosion, but they may experience pitting and crevice corrosion and undergo stress corrosion cracking in some environments.



Aluminum

Aluminum alloys are widely used in aerospace applications where their favorable strength-to-weight ratios make them the structural metal of choice. They can have excellent atmospheric corrosion capabilities. Unfortunately, the protective properties of the aluminum oxide films that form on these alloys can break down locally and allow extensive corrosion.

The highway guardrail shown on the right is located near the ocean in Florida. The aluminum alloy maintains a silvery shine except in locations where the passive film has suffered mechanical damage. The wear caused by the rail touching the wooden post at this location destroyed the passive film on the edges of the rail and allowed intergranular corrosion to proceed and cause the exfoliation corrosion shown above. While the corrosion above is very interesting, it is important to note that the railing is decades old and would have never lasted as long in this location if it were made of carbon steel.

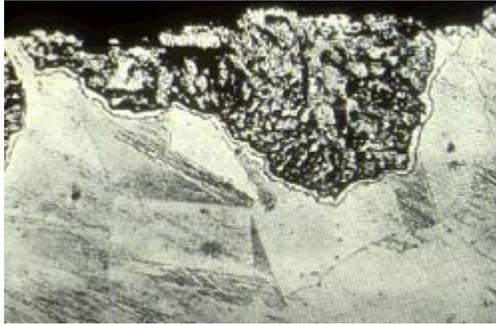


Intergranular corrosion is a major problem on airplanes and other structures made from aluminum alloys. It frequently occurs at bolt and rivet holes or at cutouts where the small grain boundaries perpendicular to the metal surface are exposed.

Copper Alloys

Brasses and bronzes are commonly used piping materials, and they are also used for valves and fittings. They are subject to stress corrosion cracking in the presence of ammonia compounds. They also suffer from dealloying and can cause galvanic corrosion

when coupled with steel and other structural metals. Most copper alloys are relatively soft and subject to erosion corrosion.



The dezincification shown above could have been controlled by using inhibited brasses which have been commercially available since the 1930's.

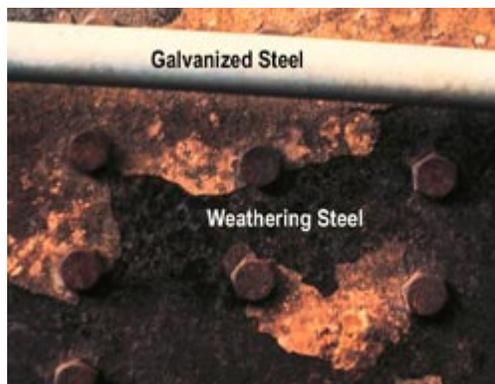
Titanium

Titanium is one of the more common metals in nature, but its limited use means that small-scale production operations result in a relatively expensive metal. In the United States it finds extensive use in the aerospace industry. The Japanese make extensive use of titanium in the chemical process industries.

There are two general types of titanium alloys-aerospace alloys and corrosion resistant alloys. The crevice corrosion of an aerospace alloy flange in a saltwater application is a classic example of how titanium gets misused.

Protective Coatings

Protective coatings are the most commonly used method of corrosion control. Protective coatings can be metallic, such as the galvanized steel shown below, or they can be applied as a liquid "paint."





Filiform corrosion occurs underneath protective coatings. The air conditioner on the left is starting to show rust stains due to problems with protective coating. The same types of problems are starting to appear on the aluminum airplane wing shown on the right.

Inhibitors and Other Means of Environmental Alteration

Corrosion inhibitors are chemicals that are added to controlled environments to reduce the corrosivity of these environments. Examples of corrosion inhibitors include the chemicals added to automobile antifreezes to make them less corrosive.

Corrosion Allowances

Engineering designers must consider how much metal is necessary to withstand the anticipated load for a given application. Since they can make mistakes, the use of the structure can change, or the structure can be misused, they usually are required to over design the structure by a safety factor that can vary from 20% to over 300%. Once the necessary mechanical load safety factor has been considered, it becomes necessary to consider whether or not a corrosion allowance is necessary to keep the structure safe if it does corrode.



The picture above shows extra steel added to the bottom of an offshore oil production platform. The one-inch of extra steel was added as a **corrosion allowance**.

Cathodic Protection

Cathodic protection is an electrical means of corrosion control. Cathodic protection can be applied using sacrificial (galvanic) anodes or by means of more complicated impressed current systems.



This Louisiana fishing boat has sacrificial zinc anodes welded to the hull to slow down corrosion. No pattern is apparent to how the anodes were attached-the design philosophy seems to be that if one anode is good, more is better.

Sources of Additional Information

Textbooks and references on corrosion include:

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This document was derived from US Government Sources

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1. An acid might have a pH near:
 - a. 3
 - b. 6.5
 - c. 7.5
 - d. 9

2. Anodes are the part of an electrochemical cell that have mostly _____ reactions.
 - a. corrosion
 - b. oxidation
 - c. neutral
 - d. reduction

3. Metals corrode because we use them in environments where they are _____.
 - a. chemically stable
 - b. exposed to passive actions
 - c. chemically unstable
 - d. anodized

4. Galvanic corrosion is an electrochemical action of two dissimilar metals in the presence of _____ and an electron conductive path
 - a. an accelerator
 - b. an electrolyte
 - c. a catalyst
 - d. a separator

5. The most anodic substance is _____:
 - a. copper
 - b. aluminum 2024
 - c. magnesium
 - d. lead

6. The most noble substance is _____:
- a. copper
 - b. aluminum 2024
 - c. magnesium
 - d. lead
7. Corrosion in concrete may be controlled by _____
- a. proper detailing to prevent cracking
 - b. keeping the water/cement ratio below 0.4
 - c. embedding the steel deep enough so that chemicals from the surface don't reach the steel
 - d. a, b, and c
8. High strength steel bolts cannot be galvanized because _____.
- a. hydrogen embrittlement may occur
 - b. stress corrosion cracking may occur
 - c. galvanic corrosion of the steel may occur
 - d. none of the above
9. True or False: Stainless steels will not stress corrode.
- a. True
 - b. False
10. When copper alloy pipe is attached to steel pipe, the steel pipe is prone to _____ corrosion:
- a. hydrogen embrittlement
 - b. crevice corrosion
 - c. galvanic corrosion
 - d. stress corrosion