

# Fundamentals of Corrosion

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Knowledge of the fundamental concepts of corrosion is necessary to understand the corrosion process. Because the scope of the corrosion concept is broad, this paper presents only the basic principles involved in the corrosion process. Those things that affect the corrosion process are defined and classified. Corrosion is divided into two classifications: wet corrosion and dry corrosion. This paper deals primarily with wet corrosion and covers the corrosion mechanism, forms of attack, and the effects of environmental factors. The basic parts of a corrosion cell are explained. Three types of corrosion cells, the principles of polarization, and the rate of corrosion are discussed. Examples are used throughout the paper to illustrate applications of the various principles. Forms of corrosion such as uniform and pitting attack are presented. Environmental influences discussed include biological corrosion, stray current, and differential environments.

Corrosion is one of the major problems facing engineers today. The seriousness of the problem is illustrated by the fact that corrosion costs \$15 billion per year in the United States. This can be further illustrated by the fact that 40 percent of the steel produced each year is used to replace corroded metal (1). Because corrosion is such a serious problem, its fundamentals must be understood.

Corrosion is "the deterioration of a substance (usually a metal) or its properties because of a reaction with its environment" (2). This deterioration can be classified into two categories: dry corrosion and wet corrosion. Dry corrosion occurs in the absence of a liquid phase or above the dew point of the environment. In this case, a metal reacts with vapors and gases usually at high temperatures. These reactions can produce a scaling and tarnishing attack on exposed metals. In wet corrosion, a metal usually reacts with aqueous solutions or electrolytes. Wet corrosion causes the greatest amount of deterioration of materials (3).

This report relates the fundamentals of corrosion and emphasizes corrosion mechanisms, forms of attack, and environmental influences. Because of the

magnitude of the subject, it is impossible to cover all aspects in detail in this paper.

## CORROSION MECHANISM

Corrosion occurs by chemical or electrochemical means. An example of a chemical reaction is the dissolving of a metal by an acid. An electrochemical reaction involves metals, chemicals, and water that combine to form cells capable of generating electricity. Through the action of these cells, metals are reverted back to their native compounds by using the electricity as a source of energy. Figure 1 shows that electrochemical cells contain four basic components: electrolyte, anode, cathode, and conductor. The electrolyte is the current-carrying medium, such as water or soil. The anode (positive electrode) is in contact with the electrolyte, and corrosion will occur through an oxidation reaction that involves the formation of ions and the release of electrons (4). The cathode (negative electrode) is also in contact with the electrolyte, but no corrosion occurs because of a reduction reaction, which is the acceptance of electrons generated from the anode (5). The conductor connects the anode and cathode to complete the circuit for current flow (4). In the wet corrosion process, all corrosion cells that are formed contain these four basic parts.

Inasmuch as the corrosion cell is electrical in nature, it operates proportional to Ohm's law, which states that "the amount of flowing current (corrosion loss) decreases as the resistance of the circuit increases and current flow increases as the potential difference between the anode and cathode increases. Thus the amount of corrosion experienced is proportional to the electrolyte's ability to react, the potential difference between anode and cathode, and the amount of resistance in the external metal circuit" (6, p. 4).

Several factors influence the electrolyte. They are ionization, resistivity, pH, and temperature. The flow of electricity through an electrolyte depends on the presence of tiny electrically charged particles called ions. These ions form the basis for the conversion of metals from a metallic form to a corroded form. Ions are formed by the addition or removal of an electron

from the basic atom. The removal of an electron yields a positively charged ion, while addition yields a negatively charged ion. Ions are also formed by dissociation, which is the breaking up or splitting of a compound into its elements. Another factor affecting the electrolyte is resistivity, which is a measure of an electrolyte's ability to resist or oppose the flow of electric current. Low resistivity means that electricity will flow freely. High resistivity means that the electrolyte is a poor conductor (7). A third factor affecting an electrolyte is the degree of acidity or alkalinity of the solution, i.e., the relative amounts of hydrogen ions, hydroxyl ions, or pH. And, finally, temperature has a pronounced effect on electrolytes. As temperature increases, the resistivity of the electrolyte is lowered. Conversely, as the temperature decreases, the resistivity increases.

Another important factor affecting a corrosion cell is the difference in potentials of the metal. The driving force for current and corrosion is the potential developed. The electromotive series (Table 1) indicates the known potentials of the various metals (3). The difference in these potentials gives some indication of their effect on the corrosion cell.

The resistance of the external circuit connecting the anode and cathode has a pronounced effect on the corrosion cell. When the resistance in this circuit is high, the rate of current flow is low and the amount of corrosion is reduced.

In the wet corrosion process there are three basic types of cells: galvanic, concentration, and electrolytic. The galvanic cell (Figure 2) is one in which the anode and the cathode are of different metals or one in which dissimilar conditions exist in the same metal (7). In this cell the electrolyte is homogeneous and the dissimilarity in the metals causes a potential difference, which induces current flow. The common flashlight battery is a good example of a galvanic cell. Current is generated by connecting the zinc case and carbon center post through a light bulb. The current flowing from the zinc case through the electrolyte filler to the carbon rod eventually corrodes the zinc, and the battery must be replaced. In the concentration cell (Figure 3), the anode and cathode are the same material while the electrolyte is nonhomogeneous (7). Current is established by different oxygen concentrations, different kinds of chemicals, or different concentrations of the same chemical in the electrolyte. The difference in the electrolyte can be illustrated by material along a buried steel pipeline. Conditions vary from wet and swampy to dry and sandy. The electrolytic cell (Figure 4) contains all the four basic components of a corrosion cell plus an external source of electric energy (7, pp. 24-48). This source is connected in the conductor between the anode and cathode to cause current flow. Corrosion takes place as an electrolytic cell when a rectifier impressing direct current is used for corrosion control on pipelines.

The three cells all contain the four basic components and induce current flow. As this current flows, deposition of hydrogen builds up a film on the cathode surface and begins to resist the flow of current. This reduction in current flow due to the resistance of the hydrogen film is known as polarization (4). If the hydrogen film is not removed either by evolution or by some reaction involving oxygen, the corrosion rate will be reduced. To understand what is happening during a corrosion process, it is helpful to know the rate at which a metal deteriorates.

Metals corrode at known rates. These rates are based on kilograms of metal lost per current discharged in a year. Some examples follow:

Metal	Rate (kg/A/year)
Lead	32.7
Zinc	10.0
Aluminum	3.6
Steel	9.1

## FORMS OF CORROSION

The many forms of wet corrosion are created by the various environments and types of corrosion mechanisms. Two of the most common forms of corrosion attack are uniform and pitting corrosion. Other forms include galvanic, crevice, intergranular, stress, fatigue, erosion, fretting, and selective leaching.

The most common form of corrosion attack is uniform corrosion. It is a chemical or electrochemical reaction that proceeds uniformly over the entire exposed surface of a large area. It occurs on metal surfaces that are homogeneous in chemical composition or that have homogeneous microstructures (8, pp. 3-32).

Another common form of attack is pitting corrosion. It is an extremely localized attack that results in holes in the metal. "A pit is defined as a cavity or hole with the surface diameter about the same as or less than the depth" (3). It is one of the most destructive forms of attack because it causes failure by perforation and only a small percentage of weight loss of the entire structure. A unique type of anodic reaction takes place in a pit. The corrosion process produces conditions that are both reactive and necessary for the continuing activity of the pit. Pitting corrosion can be initiated by metallurgical inhomogeneities. Pits are randomly distributed and have varying depth and size. Maximum pit depth information is the most useful in estimating the service life of a metal attacked in this manner (8).

Galvanic corrosion can result from the potential difference between dissimilar metals when they are in contact and surrounded by an electrolyte. This type of corrosion can produce either a uniform or pitted surface.

Crevice corrosion is localized and is caused by different concentrations of ions or dissolved gases located within crevices and other shielded areas on exposed metal surfaces. The region deep within a crevice becomes the anode and corrodes freely. A cathodic reaction takes place at the mouth of the crevice. Even in a homogeneous metal, a potential difference may exist. Metal ions are formed within a crevice, and high acidic conditions exist. This can lead to continuing activity of the corrosion process (8).

Another form of localized corrosion is called intergranular corrosion. This corrosion occurs at and adjacent to minute grain boundaries, but the grain itself experiences relatively no corrosion. Intergranular corrosion can be caused by impurities at the grain boundaries, enrichment of an element, or depletion of one of these elements in the grain boundary areas. Therefore, the grain boundary becomes anodic to the surrounding grains. As a result, the alloy at the grain boundary corrodes and may also lose its strength (3). Stainless steels that are improperly heat treated and do not contain special stabilizing alloying additions are susceptible to intergranular corrosion (8). Intergranular corrosion can be recognized by crack patterns along the grain boundaries.

The combination of tensile stress and corrosive medium produces a process known as stress corrosion. The tensile stress can be residual or external. Stress corrosion occurs in the form of intergranular or transgranular cracks. More damage is caused when the two are combined than when either acts alone. This type of corrosion usually causes failure without warning. Ex-

amples of stress corrosion are areas surrounding a weld and the stressed areas adjacent to rivets and bolts.

Corrosion fatigue is probably an extension of stress corrosion. "Fatigue is defined as the tendency of a metal to fracture under repeated cyclic stressing. Corrosion fatigue is defined as the reduction of fatigue resistance due to the presence of a corrosive medium" (3). Therefore, corrosion fatigue is related to the failure of the mechanical properties rather than to appearance.

When the rate of corrosion on a metal accelerates because of relative movement between a corrosive liquid and the metal surface, erosion corrosion occurs. It occurs in the form of grooves, gullies, waves, rounded holes, and valleys. The relative movement exposes new reactive locations on a metal, which become anodic to the relatively large surrounding cathodic area. At these locations rapid corrosion can occur. Equipment exposed to moving fluids are subject to erosion corrosion. Some of these are piping systems, valves, pumps, propellers, impellers, heat exchanger tubing, turbine blades, and equipment subject to spray (3).

Figure 1. Basic components of a corrosion cell.

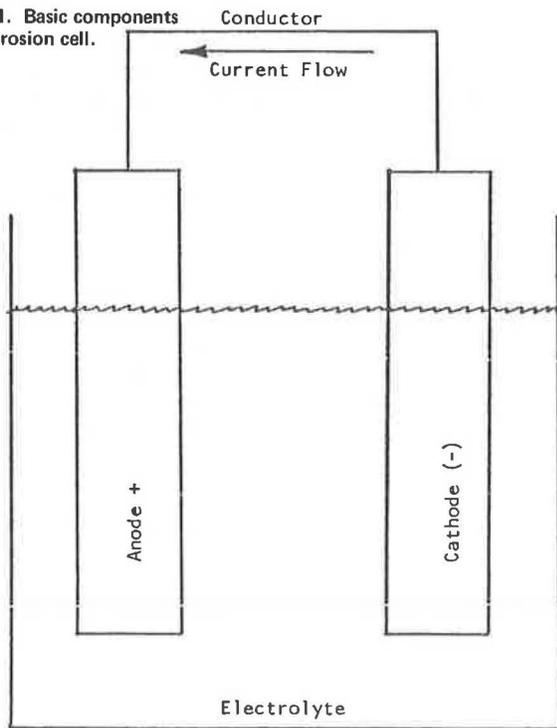


Table 1. Electromotive series.

Type	Element	Electrode Potential <sup>a</sup> (V)
Active or anodic	Magnesium	-2.363
	Aluminum	-1.662
	Zinc	-0.763
	Chromium	-0.744
	Iron	-0.440
	Cadmium	-0.403
	Nickel	-0.205
	Tin	-0.136
	Lead	-0.126
	Hydrogen	-0.000
Noble or cathodic	Copper	+0.337
	Silver	+0.799
	Platinum	+1.200
	Gold	+1.498

<sup>a</sup>Electrode potential versus normal hydrogen electrode at 25°C (77°F).

Another form of corrosion involving movement is fretting, which occurs at contact areas between materials under load subjected to vibration and slip. Fretting occurs, for example, when two parts such as bushings and bearings are closely fitted. Fretting leaves pits or grooves in the metal surrounded by corrosion products (3).

Figure 2. Galvanic cell.

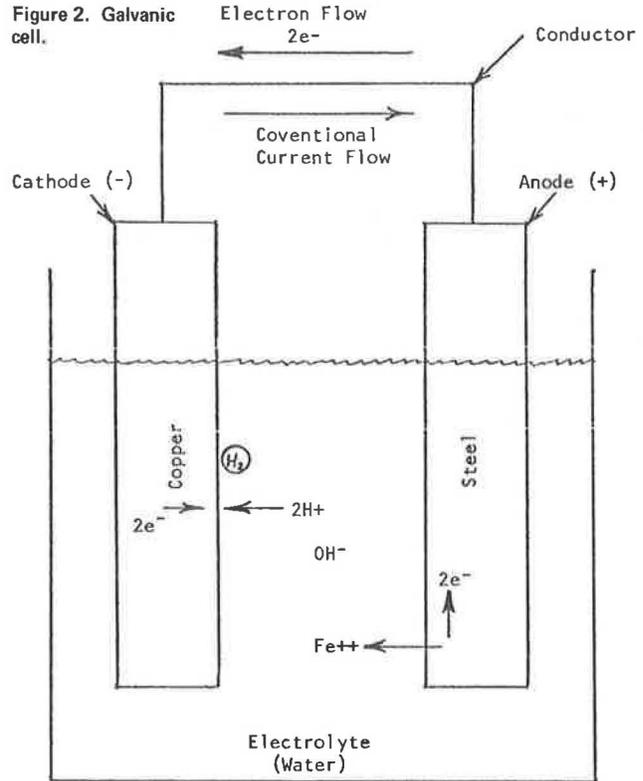


Figure 3. Concentration cell.

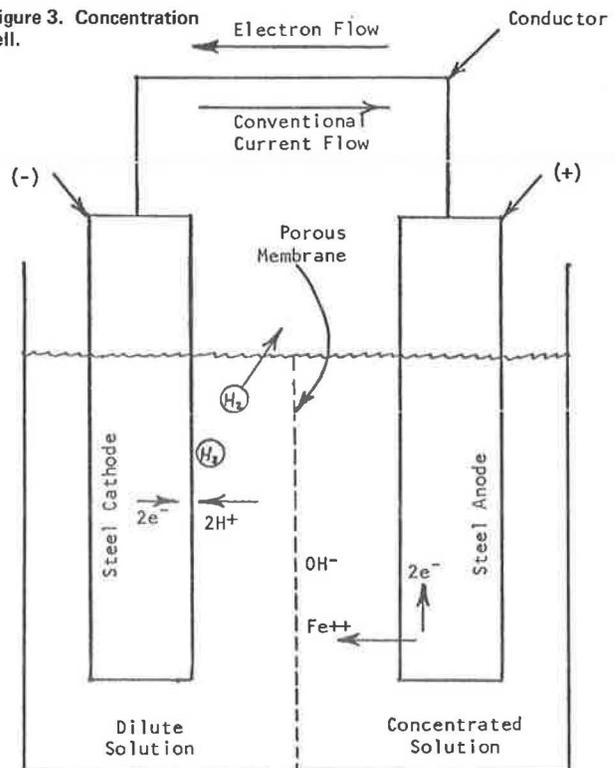
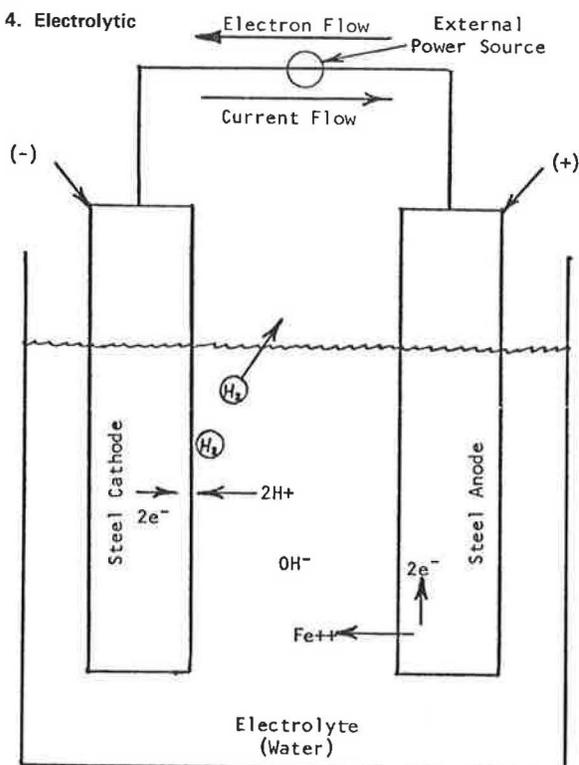


Figure 4. Electrolytic cell.



Selective leaching is a form of corrosion in which one or more elements are removed from an alloy and become electrochemically active. When an alloy consists of highly dissimilar elements, selective leaching is possible (8). One of the most common forms of selective leaching is graphitization. An example of graphitization is the removal of iron from cast iron pipe, leaving graphite.

#### ENVIRONMENTAL INFLUENCES

The forms of corrosion discussed can be influenced by the nature of their surrounding environment. An aggressive or electrochemically active environment can greatly increase the rate of corrosion of a metal. Some of the environmental factors influencing this rate are biological corrosion, stray current, and differential environments.

Biological corrosion is not actually a form of corrosion. However, the activity of living organisms (bacteria, algae) can increase the corrosion process by influencing the anodic and cathodic reactions and the protective surface films. It can also create corrosive conditions by producing deposits (3). Two types of microorganisms can cause this type of corrosion. These are aerobic (oxygen using) and anaerobic (nonoxygen using). Of the two types, anaerobic organisms are most responsible for corrosion of iron and steel.

Another environmental influence is stray current, which is caused by direct current emanating from an outside source entering and being discharged from a metal surface. At the point where stray current enters the metal surface, the area becomes the cathode. The area of discharge becomes the anode, and corrosion occurs. Sources of stray direct current include electric railways, railroad signal systems, cathodic protection systems for pipelines, direct current industrial generators, and direct current welding equipment. Under certain conditions, alternating currents can become partially rectified by passing through and off of metal structures,

and the partial direct current component can cause corrosion.

Differential environment also affects the corrosion process. It occurs as a concentration cell when a metal is in contact with an electrolyte that varies in composition from point to point or varies in concentration from point to point along the surface of the metal. Examples of these variations in environments include the conditions present along a buried pipeline, a steel pipe in contact with both soil and water, or the interface between a steel reinforcing bar and the surrounding concrete.

#### SUMMARY

This paper discusses the fundamentals of corrosion. The paper defines terms and basic electrochemical principles that determine the corrosion process. These definitions should not be considered the only correct ones. Other definitions can be found that may be as good or even better. The principles of corrosion mechanism, forms of attack, and environmental influences have been used to simplify the various aspects of corrosion.

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