Corrosion Theory and Protection

An Online Continuing Education Course for Engineers

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Credit: 1 Hour / 1 PDH / 1 CPD

Corrosion Theory and Protection

Introduction

The annual cost of corrosion and corrosion protection in the United States is estimated by the National Association of Corrosion Engineers (NACE) to be in excess of 10 billion dollars. This figure is perhaps less intimidating considering that corrosion occurs, with varying degrees and types of degradation, whenever metallics are used.

Corrosion can be mitigated by five basic methods: coatings, cathodic protection, materials selection, chemical inhibitors, and environmental change. A basic understanding of corrosion will enable you to comprehend how these methods help prevent corrosion, and it will establish an overall introduction to the purpose for the entire engineer manual on painting.

Causes of Corrosion

Corrosion is defined as the deterioration of a material, usually a metal, because of a reaction with its environment and which requires the presence of an anode, a cathode, an electrolyte, and an electrical circuit. To understand the application of protective coatings or cathodic protection in corrosion control, the basic concepts of corrosion of metals in the presence of moisture needs to be reviewed.

a. Corrosion occurs by an electrochemical process. The phenomenon is similar to that which takes place when a carbon-zinc “dry” cell generates a direct current. Basically, an anode (negative electrode), a cathode (positive electrode), an electrolyte (environment), and a circuit connecting the anode and the cathode are required for corrosion to occur (see Figure 1). Dissolution of metal occurs at the anode where the corrosion current enters the electrolyte and flows to the cathode. The general reaction (reactions, if an alloy is involved) that occurs at the anode is the dissolution of metal as ions:

$$M \rightarrow M^{n-} + e^{n-}$$

where

M = metal involved
n= valence of the corroding metal species
e = electrons

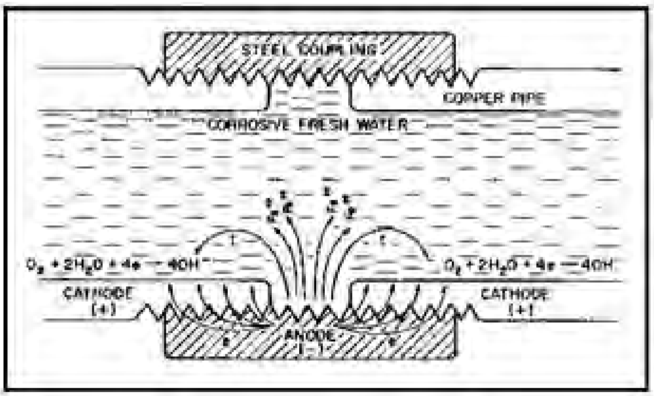

Figure 1. The basic corrosion cell consists of an anode, a cathode, an electrolyte, and a metallic path for electron flow. Note that the corrosion current (ζ) enters the electrolyte at the anode and flows to the cathode

Examination of this basic reaction reveals that a loss of electrons, or oxidation, occurs at the anode. Electrons lost at the anode flow through the metallic circuit to the cathode and permit a cathodic reaction (or reactions) to occur. In alkaline and neutral aerated solutions, the predominant cathodic reaction is

$$O_2 + 2H_2O + 4e \rightarrow 4(OH)$$

The cathodic reaction that usually occurs in deaerated acids is

$$2H^- + 2e^- \rightarrow H_2$$

In aerated acids, the cathodic reaction could be

$$O_2 + 4H^- + 4e^- \rightarrow 2H_2O$$

All of these reactions involve a gain of electrons and a reduction process.

b. The number of electrons lost at the anode must equal the number of electrons gained at the cathode. For example, if iron (Fe) was exposed to an aerated, corrosive water, the anodic reaction would be

$$Fe \rightarrow Fe^{--} + 2e^-$$

At the cathode, reduction of oxygen would occur

$$O_2 + 2H_2O + 4e^- \rightarrow 4(OH^-)$$

Because there can be no net gain or loss of electrons, two atoms of iron must dissolve to provide the four electrons required at the cathode. Thus, the anodic and cathodic reactions would be

$$2\ Fe \rightarrow 2Fe^{--} + 4e^{-} \text{ (anodic)}$$

$$O_2 + 2H_2O + 4e^{--} \rightarrow 4(OH^{-}) \text{ (cathodic)}$$

These can be summed to give the overall oxidation-reduction reaction

$$2Fe + O_2 + 2H_2O \rightarrow 2Fe^{--} + 4(OH^{-})$$

c. After dissolution, ferrous ions (Fe^{++}) generally oxidize to ferric ions (Fe^{+++}); these will combine with hydroxide ions (OH^{-}) formed at the cathode to give a corrosion product called rust ($FeOOH$ or Fe_2O_3 x H_2O). Similarly, zinc corroding in an aerated, corrosive water (i.e., $Zn \rightarrow Zn^{++} + 2e^{-}$) will form the corrosion product $Zn(OH)_2$. The important issue to remember is that anodic dissolution of metal occurs electrochemically; the insoluble corrosion products are formed by a secondary chemical reaction.

Forms of Corrosion

Almost all corrosion problems and failures encountered in service can be associated with one or more of the eight basic forms of corrosion: general corrosion, galvanic corrosion, concentration-cell (crevice) corrosion, pitting corrosion, intergranular corrosion, stress corrosion cracking, dealloying, and erosion corrosion.

a. General corrosion. With general corrosion (sometimes called uniform corrosion), anodic dissolution is uniformly distributed over the entire metallic surface. The corrosion rate is nearly constant at all locations. Microscopic anodes and cathodes are continuously changing their electrochemical behavior from anode to cathode cells for a uniform attack. The general corrosion rates for metals in a wide variety of environments are known, and common practice is to select materials with rates that are acceptable for the application.

b. Galvanic corrosion.

(1) Galvanic (dissimilar metals) corrosion occurs when two electrochemically dissimilar metals are metallically connected and exposed to a corrosive environment. The less noble metal (anode) suffers accelerated attack and the more noble metal (cathode) is cathodically protected by the galvanic current. The tendency of a metal to corrode in a galvanic cell is determined by its position in the "galvanic series" of metals and alloys as listed in Table 1.

Table 1
Galvanic Series in Seawater at 25 °C (77 °F)

Corroded end (anodic, or least noble)
Magnesium
Magnesium alloys
Zinc
Galvanized steel or galvanized wrought iron
Aluminum alloys - 5052, 3004, 3003, 1100, 6053, in this order
Low-carbon steel
Wrought iron
Cast iron
Ni-Resist (high-nickel cast iron)
Type 410 stainless steel (active)
50-50 lead-tin solder
Type 450 stainless steel (active)
Type 304 stainless steel (active)
Type 316 stainless steel (active)
Lead
Tin
Copper alloy C28000 (Muntz metal, 60% Cu)
Copper alloy C67500 (manganese bronze)
Copper alloys C46400, C46500, C46600
Alloy 200 (active)
Alloy 6700 (active)
Alloy B
Chlorimet 2
Copper alloy C27000 (yellow brass, 65% Cu)
Copper alloys C44300, C44400, C44500 (admiralty brass)
Copper alloys C60800, C61400 (aluminum bronze) Copper alloy C23000 (red brass, 85% Cu)
Copper C11000 (ETP copper)
Copper alloys C65100, C65500 (silicon bronze)
Copper alloy C71500 (copper nickel, 30% Ni)
Copper alloy C92300, cast (leaded tin bronze G) Copper alloy C92200, cast (leaded tin bronze M) Alloy 200 (passive)
Alloy 600 (passive)
Alloy 400
Type 410 stainless steel (passive)
Type 304 stainless steel (passive)
Type 3316 stainless steel (passive)
Alloy 825
Alloy 62
Alloy C
Chlorimet 3
Silver
Titanium
Graphite
Gold
Platinum
Protected end (cathodic, or most noble)

(2) The metal order listed in Table 1 is only appropriate for seawater at 25 °C (77 °F). The order

may vary with both temperature and composition of the electrolyte (water or soil). In fact, under some conditions, two metals may reverse their water respective order (potentials). For example, iron may become anodic with respect to zinc in fresh water at a temperature above 66 °C (150 °F).

(3) A common galvanic corrosion cell occurs when copper lines are connected to galvanized steel water mains. In this example, the soil is the electrolyte, the copper line is the cathode, and the water main is the anode.

c. Concentration-cell corrosion. Concentration-cell corrosion occurs because of differences in the environment surrounding the metal. This form of corrosion is sometimes referred to as "crevice corrosion," "gasket corrosion," and "deposit corrosion" because it commonly occurs in localized areas where small volumes of stagnant solution exist. Normal mechanical construction can create crevices at sharp corners, spot welds, lap joints, fasteners, flanged fittings, couplings, threaded joints, and tube sheet supports. At least five types of concentration cells exist; the most common are the "oxygen" and "metal ion" cells. Areas on a surface in contact with an electrolyte having a high oxygen concentration generally will be cathodic relative to those areas where less oxygen is present (oxygen cell). Areas on a surface where the electrolyte contains an appreciable quantity of the metal's ions will be cathodic compared to locations where the metal ion concentration is lower (metal ion cell).

d. Pitting corrosion. Pitting corrosion is a randomly occurring, highly localized form of attack on a metal surface, characterized by the fact that the depth of penetration is much greater than the diameter of the area affected. Pitting is one of the most destructive forms of corrosion, yet its mechanism is not completely understood. Steel and galvanized steel pipes and storage tanks are susceptible to pitting corrosion and tuberculation by many potable waters. Various grades of stainless steel are susceptible to pitting corrosion when exposed to saline environments.

e. Intergranular corrosion. Intergranular corrosion is a localized condition that occurs at, or in narrow zones immediately adjacent to, the grain boundaries of an alloy. Although a number of alloy systems are susceptible to intergranular corrosion, most problems encountered in service involve austenitic stainless steels (such as 304 and 316) and the 2000 and 7000 series aluminum alloys. Welding, stress relief annealing, improper heat treating, or overheating in service generally establish the microscopic, compositional inhomogeneities that make a material susceptible to intergranular corrosion.

f. Stress corrosion cracking. Stress corrosion cracking (environmentally induced-delayed failure) describes the phenomenon that can occur when many alloys are subjected to static, surface tensile stresses and are exposed to certain corrosive environments. Cracks are initiated and propagated by the combined effect of a surface tensile stress and the environment. When stress corrosion cracking occurs, the tensile stress involved is often much less than the yield strength of the material; the environment is usually one in which the material exhibits good resistance to general corrosion.

g. Dealloying. Dealloying is a corrosion process in which one element is preferentially removed from an alloy. This occurs without appreciable change in the size or shape of the component; but the affected area becomes weak, brittle, and porous. The two most important examples of dealloying are the preferential removal of zinc from copper-zinc alloys(dezincification), and the preferential removal of iron from gray-cast iron (graphitic corrosion). Graphitic corrosion sometimes occurs on underground cast iron water mains and leads to splitting of the pipe when the water pressure is suddenly increased.

h. Erosion corrosion. Erosion corrosion refers to the repetitive formation (a corrosion process) and destruction (a mechanical process) of the metal's protective surface film. This typically occurs in a moving liquid. Erosion may be impinging (in the case of a pipe ell) or sliding (pipe wall) when it occurs An example is the. erosion corrosion of copper water tubes in a hot, high velocity, soft water environment. Cavitation is a special form of erosion corrosion.

Corrosion Mitigation

Corrosion mitigation can be accomplished by design considerations, by employing corrosion-resistant materials of construction, by employing cathodic protection, by using protective coatings, or by using inhibitors.

a. Design considerations. The use of acceptable engineering practices to minimize corrosion is fundamental to corrosion control. This is accomplished by engineering design. One of the most important factors in designing for corrosion control is to avoid crevices where deposits of water-soluble compounds and moisture can accumulate and are not accessible for maintenance. Any region where two surfaces are loosely joined, or come into proximity, also qualifies as a crevice site. Joining geometries also present various crevice corrosion problems. Examples include: bolting, back-to-back angles, rough welds, weld spatter, sharp edges, corners, discontinuities, and intermittent welding.

(1) Crevice corrosion. Crevice corrosion relies on establishing a crevice geometry to allow water or other liquids or deposits to enter the crevice. One form of corrosion prevention is to eliminate crevice geometry by design. Joints and fastenings should be arranged to give clean, uninterrupted lines; therefore, welded joints are preferable to bolted or riveted joints. Sound welds and complete weld penetration will help to avoid porosity and crevice development that often result from intermittent welding, rough welds, and weld spatter. Grinding sharp edges, corners, welds, and weld spatter will help prevent crevice corrosion, as well as paint striping procedures over similar surfaces. Striping is a procedure that entails brush or spray application of the primer or, in some instances, the entire coating system over potential corrosion sites. Striping is designed to give additional barrier protection from the exposure, and it is common when the service environment includes some degree of immersion or splash.

(2) Stainless steel coupled to carbon steel. The galvanic series listed in Table 1 illustrates some of the common metals in seawater. The further apart the metals are in the series, the more rapid the corrosion of the more anodic metal will be. That is, a metal tends to corrode when connected to a more cathodic metal. For example, carbon steel will corrode more rapidly when connected to stainless steel.

(3) Stainless steel—active and passive states.

(a) Several grades of stainless steel appear toward the anodic (upper) end of the galvanic series when they are in the “active” condition, and at the cathodic (lower) end when they are in the “passive” condition. The corrosion-resistant nature of stainless steel is related to its inherent ability to form a protective oxide film in the presence of oxygen or various oxidizing chemicals such as nitric or sulfuric acid.
If the protective oxide film is destroyed, the stainless steel is subjected to rapid corrosion (the active condition) in the presence of oxygen-free acids such as hydrochloric acid. Therefore, the correct application of a specific grade of stainless steel should include a determination if the oxidation level of the environment will result in a passive or active state.

(b) Stainless steels, particularly the 300 series, are subject to a heat treating effect called “sensitization” during welding and stress relieving between 427 °C (800 °F) and 760 °C (1400 °F). During welding, these stainless steels may form chromium carbides (at temperatures of 427 °C (800 °F) to 760 °C (1400 °F). Therefore, the chromium near the grain boundaries is tied up and no longer forms the protective oxide film (chromium oxide). Thus, the grain boundaries are susceptible to intergranular corrosion and the stainless steel is no longer in the passive state. Sensitized stainless steels can deteriorate in acidic soil or water. This type of corrosion can be prevented by a solution treatment and repassivation process after welding.

(4) Unfavorable area differences. The rate of corrosion resulting from galvanic action frequently will depend on the relative exposed areas of the two metals in contact. For example, zinc will corrode when connected to iron. The zinc will “protect” the iron by making it the cathode of the galvanic cell. This is the principle behind a zinc-rich coating on steel. Small anode areas, in combination with large cathode areas, should be avoided whenever possible. A small piece of zinc will corrode rapidly when coupled to a large area of iron, yet the iron will receive little protection. Coating less noble metals and leaving the more noble metal uncoated is not recommended. A poor coating application can reduce the service life of the metal significantly because of local defects which will cause accelerated anodic corrosion resulting from a galvanic action. Examples of these coating defects are pinholes, scratches, skips, and physical damage.

(5) Isolation of dissimilar metals. Galvanic attack may be prevented by using an insulator to prevent contact (completion of electrical circuit) between dissimilar metals. The more noble metal can be insulated from the less noble metal through the use of plastic

washers for fasteners. Ceramics or nonconductive insulating materials also may be used.

(6) Connection of old and new materials. Galvanic corrosion is not limited to cells in which totally dissimilar metals are in contact and exposed to an electrolyte. Differences in the composition or surface condition of “similar” metals frequently can result in galvanic corrosion cells. For example, clean steel is typically anodic to corroded steel. Therefore, it is common in pipeline operations to find new pipeline installed in a repaired section or branch line corroding more rapid
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of the anodic sites. The entire protected structure becomes cathodic relative to the auxiliary anodes. Therefore, corrosion of the metal structure will cease when the applied cathodic current equals the corrosion current. There are two basic methods of corrosion control by cathodic protection. One involves the use of current that is produced when two electrochemically dissimilar metals or alloys (T etallically connected and
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