

Material Matters

Galvanic or Dissimilar Metals Corrosion (Part 1)

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Introduction

It was Luigi Galvani who discovered the dissimilar metal energy force in 1791, through a series of experiments with the exposed nerves of a frog leg that twitched and contracted when connected to a metal. In fact, he found that two dissimilar metals produced an even larger effect than one metal alone. This effect, called the galvanic effect, is something many who have amalgam tooth fillings have experienced directly while eating; when a sudden electrical sensation is felt as a fork touches a filling. The contact of dissimilar metals, in the weak electrolyte of oral fluids, creates a weak battery, and the voltage generated is enough to create a mild electrochemical reaction. The principle was later put to practical use by Alessandro Volta who constructed the first electrical cell, or battery in 1800: a series of silver and zinc metal disks, separated by cloth soaked in a salt solution.⁽¹⁾ This is the basis of all modern wet-cell batteries.

The science of cathodic protection (CP) was nurtured in 1824, when Sir Humphrey Davy made a presentation to the Royal Society of London regarding the rapid decay of copper sheeting on the Royal Navy's war ships. In January 1824 Davy put forth his findings that iron or copper, and for that matter any metal in saltwater where oxygen is present, forms a galvanic corrosion cell and one metal or the other is gradually dissolved. He advocated a small quantity of zinc, or even malleable iron should be used in contact with copper to prevent its corrosion. Davy found that small "protectors" of malleable iron preserve the copper by the iron gradually dissolving in a galvanic process.⁽²⁾

Sir Humphrey Davy and Michael Faraday engineered the galvanic principals into the useful protection of metallic structures in the early part of the nineteenth century. The sacrificial use of one metal to protect another is still a widespread method of cathodically protecting metallic structures practiced today.

The Galvanic Corrosion Cell

Corrosion of metals is an electrochemical process in which electrons migrate from one site to another undergoing an oxidation-

reduction reaction. Some metals, such as platinum, silver, and gold, are relatively inert in their natural states. Those that are refined or reduced from ores are thermodynamically unstable, and tend to oxidize back to their natural states according to their activity, or electromotive force.⁽³⁾ The basic components required for the corrosion reaction are an anode (where metal corrodes and oxidation occurs); a cathode (where reduction occurs); an electrolyte or conductive solution; and a metallic connection contact or conductive electrical path between the anode and cathode as shown in Figure 1.

Galvanic corrosion (also called "dissimilar metal corrosion") refers to corrosion damage induced when two dissimilar metals, or conducting non-metal such as graphite, are electrically coupled in an electrolyte. Corrosion is accelerated when these materials come into contact with one another in the same electrolyte – an electrochemical condition known as a galvanic corrosion cell. This is illustrated in Figure 1.

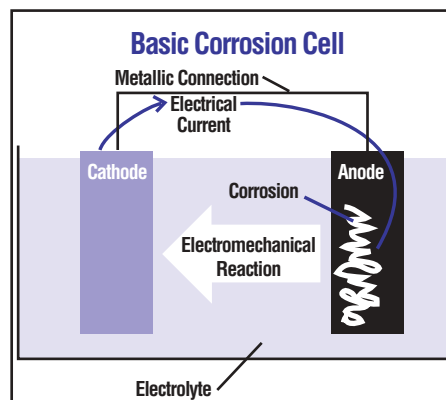


FIGURE 1. Basic Galvanic Corrosion Cell

The driving energy force for current flow and galvanic corrosion is the potential or voltage difference developed between conductive materials. When dissimilar metals are placed in contact, they can produce a voltage, as in a battery or electrochemical cell. The potential difference causes electrons to flow between them while they are electrically coupled in a conductive solution. The direction of current flow, and therefore the galvanic behavior, depends upon which metal or alloy is more active or electro-negative.

The dry cell battery shown in Figure 2 is a good example of a galvanic corrosion cell. The carbon electrode acts as a noble corrosion resistant material - the cathode, while the zinc casing is the anode, which actively corrodes. The moist paste between these two

electrodes provides the conductive (and corrosive) electrolyte environment that carries the flow of ionic current. Once the electrical circuit is completed current flows.

When coupled to form a galvanic corrosion cell, metals toward the more positive potential or noble direction of the galvanic series will react cathodically (support the reduction reactions and be protected from corrosion); while those toward the more negative or active direction will react anodically (be oxidized and readily corrode). The further apart the metals are in potential, the stronger the galvanic effect, the faster the anode corrodes, and the greater the protection provided to the cathode. Corrosion attack on the less resistant material is increased while attack on the more resistant material is decreased, as compared to the behavior of these metals when they are not in electrical contact.

The extent of accelerated corrosion resulting from galvanic coupling is affected by the following factors:

- The potential or voltage difference between the materials;
- The polarization behavior of the materials;
- The geometric and area relationship of the anode to cathode surfaces.
- The nature and conductivity of the electrolyte environment;

The two major factors affecting the severity of galvanic corrosion are (1) the voltage difference between the two metals, and (2) the size ratio of the exposed area of the cathodic metal relative to that of the anodic metal. The natural differences in metal potentials produce galvanic differences, such as a galvanic series.

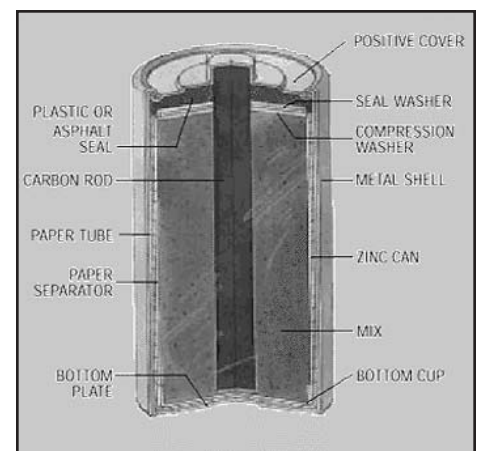


FIGURE 2. Dry Cell Battery - Galvanic Corrosion Cell

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Galvanic Series in Seawater

A galvanic series of metals and alloys (See Figure 3) is useful for predicting galvanic relationships. One way to predict whether a galvanic corrosion process will actually occur is through the use of a galvanic series, which provides an arrangement of various conductive metals according to their electrical potentials, measured in a specific electrolyte (e.g. flowing seawater). This allows one to determine which metal or alloy in a galvanic couple is more active or more noble. The separation between the two metals or alloys in the galvanic series provides an indication of the magnitude of galvanic corrosion potential. These series illustrate only the tendency towards corrosion; they do not predict a rate of corrosion. Galvanic series are available for other electrolytes, but seawater is the one most commonly known.

The "Galvanic Series in Seawater" shown in Figure 3, lists metals and alloys ranked in order of their electrical potential in flowing seawater. In a galvanic couple involving any two or more metals from the list, the one closer to the more negative (anodic or active) potential end of the series will corrode faster, while the one toward the more positive (cathodic or passive) potential end will corrode slower or not at all. Metals with more positive corrosion potentials are called cathodic, noble, or passive; while those with more negative corrosion potentials are referred to as, anodic or active metals. This galvanic series provides an indication of the potentials established when dissimilar metals are placed in contact with each other in seawater.

For example, suppose an aluminum alloy with an average potential of -0.90 volt is coupled to an AISI type 316 stainless steel with an average potential of -0.05 volt. The Galvanic Series predicts that the aluminum will be the anode and corrode, with the potential difference between the two alloys about 0.85 volts. It is this voltage difference or potential that drives the flow of electrons to accelerate corrosion of the anodic metal, and protect the cathodic metal.

When different conductive materials are welded, bolted, or otherwise joined in an electrolyte, the corrosion rate of the active (anodic) material is increased, while the corrosion rate of the passive (cathodic) metal is decreased. The galvanic series helps determine which coupled material is active and which is passive.⁽⁴⁾ While there is a general tendency for the active metals to corrode more rapidly than the passive metals, there are exceptions. The

galvanic series only considers electrical potential. There are many other variables that affect corrosion.

The potential of a metal or alloy is affected by many environmental factors. There is no absolute value of potential for a given metal independent of variables that influence the corrosive characteristics of the solution (electrolyte) in which the potential is measured. Since a galvanic series can be very different in other environments, this requires a series be determined for each environment of interest.⁽⁵⁾ Typically, the "Galvanic Series" that most are familiar with has been created from measurements in flowing seawater. If potentials of metals are measured in other fluids (electrolytes) and listed in order of their potentials, a galvanic series for that environment can also be developed.

A word of caution: There may be shifts in the potential positions of various metals in a galvanic series for different fluids. Metals can behave very differently in other environments; that is, the relative potential position of metals and alloys in a galvanic series can change from one environment to another. In fact, variations within the same environment may occur with changes in such variables as pH, temperature, solution strength, polarization, degree of agitation or aeration, etc. Thus, corrosion product films and other changes in surface composition can occur in some environments and therefore, no one potential value can be given for any particular metal.⁽⁶⁾ Consequently, there is no way, other than by direct potential measurements in each environment of interest, to determine the electrical potentials and direction of any galvanic effects.

For example, zinc is normally negative to steel at ambient temperatures. However, the potential difference decreases with increasing temperature until the potential difference is zero or even reverse.

However, the relative tendencies of metals to corrode remains about the same in many environments in which they are likely to be used. Therefore, their relative positions in the seawater galvanic series can be similar in other environments as well. Since more observations of potentials and galvanic behavior have been made in seawater than in any other environment, this series is often used as an approximation of the probable direction of galvanic effects in other environments in the absence of more reliable information.⁽⁷⁾

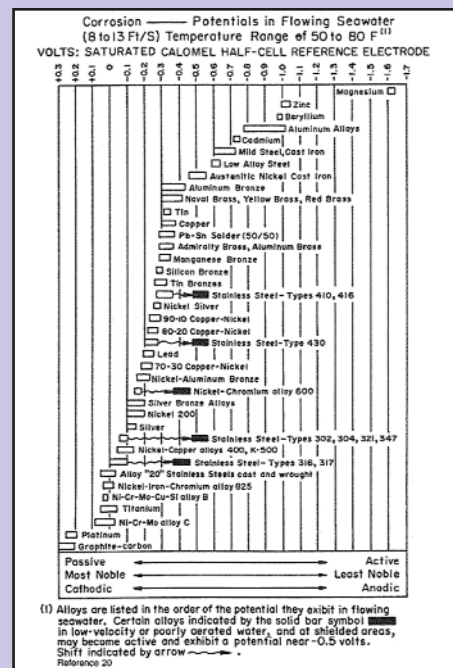


FIGURE 3. Galvanic Series in Flowing Seawater

Several metals in the seawater galvanic series list are grouped. The potential differences within a group are insignificant, and the metals can be combined without significant galvanic effects. A general rule of thumb is that as long as the potential differences are within 0.25 volt, galvanic effects should be minor, and the metals or alloys are considered compatible.

Part 2 of Galvanic Corrosion by S. Morrow will be published in the Spring 2003 issue.

(1) Philip J. Bromberg, Physical Chemistry, Second Edition, Allyn and Bacon, Inc. 1984, Newton, Massachusetts 02157, p 300.

(2) Source: "On the corrosion of copper sheeting by seawater, and on methods of preventing this effect, and on their application to ships of war and other ships", Proceedings of the Royal Society, 114 (1824), pp 151-246 and 115 (1825), pp 328-346.

(3) Lela E.Buis, "Improved Design For Corrosion Control", Materials Performance, November 1989, NACE International, pp 37-39.

(4) Arthur H. Tuthill, "Managing Galvanic Corrosion", Materials Performance, February 1995, NACE International, pp79-84.

(5) "Corrosion Basics", Materials Performance, April 1991, NACE International, p 70.

(6) Gregory Kobrin, "Materials Selection", ASM Metals Handbook, Ninth Edition, Volume 13, Corrosion, 1987, ASM International, p 324.

(7) "Corrosion Basics", Materials Performance, April 1991, NACE International, p 70.