CORROSION:
Costs, Causes, and Cures

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Corrosion is best defined as "the process by which a material, usually a metal, combines with certain elements within it's environment to produce a product that does not retain the useful properties of the original material". Unfortunately, this seemingly innocuous textbook definition does not convey the economic losses that result from corrosion damage. The minimum financial losses due to this "process" are well in excess of the combined annual costs of fires, floods, hurricanes, tornadoes, and earthquakes in North America.

Let us examine some statistics to see how such enormous losses can be accumulated. In 1949, the direct cost of corrosion in the United States was estimated to be $5 billion a year. More recent surveys in 1971, undertaken by T.P. Hoar in England on behalf of the Department of Trade and Industry, suggested that direct losses due to corrosion could be 1.25 percent of the gross national product. A recent estimate of the National Commission on Materials Policy in the United States comes up with the figure $15 billion a year, whereas using Hoar's percentage of GNP in the U.S., losses would actually approach $30 billion a year in the United States.

A National Bureau of Standards report in 1966 stated that 40 percent of U.S. steel production was used to repair or replace items rendered useless due to corrosion. At that time, this amounted to 40 million tons of steel a year. Fifty percent of the world's zinc production is sacrificed to protect steel. Sixteen cents on every barrel of crude oil is spent on corrosion losses. Corrosion costs the oil and gas industry an estimated $200 per mile of line pipe per year on over one million miles of underground pipelines in the United States.

Most catastrophic industrial failures have corrosion among their causes. In many cases, corrosion is found to be the principal factor leading to structural or mechanical breakdown. The United States chemical industry estimates the annual costs due to stress corrosion cracking failures alone to be in the order of $30 million a year. In 1968, the United States Air Force determined that 38 percent of their aircraft accidents, major and minor, were attributable to corrosion.

The economics of reducing this wastage is sound. However, equally important is that some of this waste results in the dispersion of essential materials and energy in such a manner that they cannot be practically recovered for recycling.

Danger to human life results from, among other things, corroded equipment releasing toxic substances into our environment.

The above statistics should not be startling as, unless preventative measures are undertaken, 100 percent of all existing refined metals will eventually corrode. To prevent this devastating occurrence, design engineers, maintenance, and management personnel must understand the basics of the corrosion process, in order to counteract its destructive powers - and these same people must be prepared to invest some capital, as corrosion control also costs money.

WHY METALS CORRODE

Electrochemical reactions will only occur spontaneously if the free energy of the products is less than that of the reactants. In other words, materials are only completely stable if they have attained the product which possesses the minimum possible free energy.

During the refining of a metal such as steel, the iron is divorced from its associated oxygen in a blast furnace, and an enormous amount of energy is put into the steel in the form of heat (approximately 28-35 million BTU's is required to produce one ton of steel). As long as it remains metallic, a piece of steel retains a small portion of this energy, bound up within itself, always urging the metal to corrode back to the ore from which it was unwillingly derived.

It is this energy which supplies the power to drive the various corrosion reactions. When steel rusts, the latent energy is released and the metal, relieved of its uneasy hypertension, thankfully reverts to a stable oxide again and the cycle is complete.

The energy which is released in the corrosion process is called Gibbs free energy, and is expressed in calories or kilo calories per mole in most textbooks. Table 1 shows the free energy of formation of some oxides, expressed in kilo calories/mole of oxide at 27ºC (unless otherwise indicated).

Oxide Type	Kilo Calories per Mole	Temp.
Silver	2.55	
Copper	34.6	
Lead	45.0	
Nickel	51.4	
Iron	54.6	227ºC
Zinc	76.2	
Magnesium	136.5	
Quartz	197.3	
Chromium	236.7	227ºC
Aluminium	377.6	

TABLE 1 • Free Energy of Formation of Some Oxides

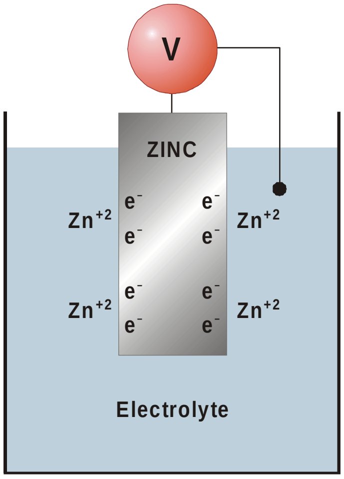


FIGURE 1 • Electrochemical Equilibrium Resulting in Solution Potential of Zinc

ACTIVE	Magnesium
	Zinc
	Alclad 3S
	Aluminium 3S
	Aluminium 61S
	Aluminium 63S
	Aluminium 52
	Low Steel
	Alloy Steel
	Cast Iron
(ELECTRONEGATIVE)	Type 410 (Active)
	Type 430 (Active)
	Type 304 (Active)
	Type 316 (Active)
	Ni-Resist
	Muntz Metal
	Yellow Brass
	Admiralty Brass
	Aluminium Brass
	Red Brass
	Copper
	Aluminium Bronze
	Composition G Bronze
	90/10 Copper-Nickel
	70/30 Copper-Nickel - Low Iron
(ELECTROPOSITIVE)	70/30 Copper-Nickel - High Iron
	Nickel
	Inconel
	Silver
	Type 410 (Passive)
	Type 430 (Passive)
	Type 304 (Passive)
	Type 316 (Passive)
	Monel
	Hastelloy C
NOBEL	Titanium

TABLE 2 • Galvanic Series of Metals and Alloys in Sea Water

In Table 1, it can be seen that substances like silver have low free energies and sometimes appear as native silver in ores, and some, such as aluminium, have such large free energies that their recovery from ores on a commercial scale has only been achieved in this century.

If a small sample of metal (say zinc) is immersed in a neutral pH aqueous solution, some of the metal will immediately dissolve by the reaction:

$$\mathrm{Zn} \rightarrow \mathrm{Zn}^{+2} + 2e^{-} \tag{1}$$

The two electrons remain behind in the metal. An equilibrium is soon established due to the electrical charge separation of the zinc ions and the electrons. This results in a potential difference between the metal and its environment, referred to as the solution potential (Figure 1).

There is an important relation between Gibbs free energy and solution potential expressed by the equation:

$$\Delta G = -EnF \tag{2}$$

where:

E = the electrode (corroding element) potential

n = the number of electrons (chemical equivalents) in the reaction

F = Faraday's number which relates the weight of metal going into solution with coulombs of charge transferred

The principle consideration of this relationship for the nonelectrochemist is the relationship between energy and measurable solution potential. The equation indicates that a metal with a large free energy will have a large negative solution potential.

If pure metals are placed in aqueous solution of their salts under controlled conditions, each metal exhibits an electrical potential when compared to a reference electrode. These metals can be arranged into what is known as the electrochemical series. With the electronegative metals at the top and the electropositive metals at the bottom.

A similar series can be made using commercial metals and alloys immersed in sea water. This series is called the practical or galvanic series and is reproduced in Table 2.

If a dissimilar metal, such as copper, is placed in the same solution as the zinc, without an electrical connection between the two electrodes, the copper will establish an independent equilibrium with the solution, as did the zinc.

A voltmeter connected between the two metals will indicate the difference of solution potentials between the two metals (approximately 0.9V in sea water). If the electrodes are interconnected by a metallic path, the individual electrode equilibriums are disrupted. The different solution potential of the zinc and copper results in a current flow through the cell. The current will flow, from the copper to the zinc through the metallic path and from the zinc to the copper through the electrolyte (solution). Current entering the solution from the zinc will cause the reaction expressed in Equation 1 to continue, resulting in continuous corrosion of the zinc (Figure 2).

Several possible reactions can occur at the copper electrode. However, the dissolution (corrosion) of copper will stop.

The area of corrosion (zinc electrode) is called the anode (location of oxidation) and the location not corroded (copper electrode) is called the cathode (location of reduction).

If two metals from the galvanic series are coupled together in an aqueous solution, the metal higher in the series (more electronegative or active) will become the anode or corroding element in this cell, and the metal that is lower is the series (electropositive or more noble) will become the cathode or noncorroding element. A metal that is the anode in one combination can become the cathode in another combination. (Table 3)

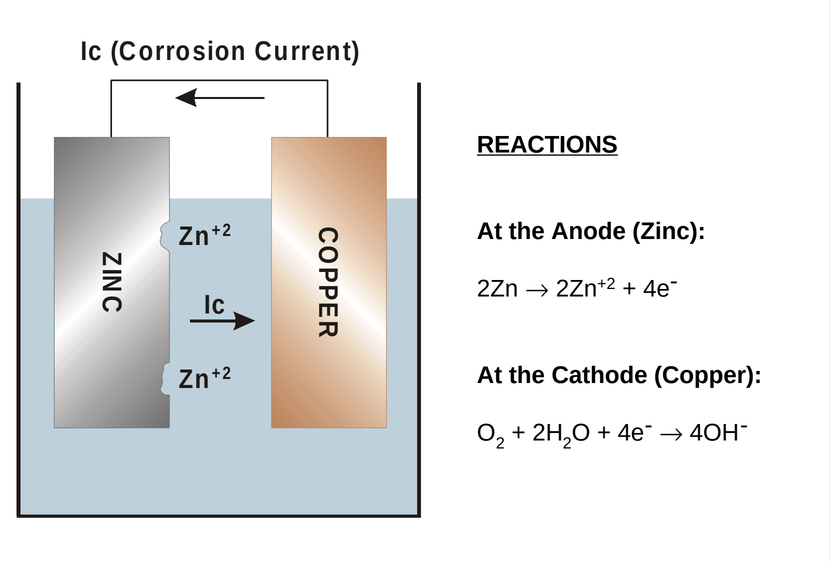


FIGURE 2 • Simple Electrochemical Corrosion Cell

Metal	Volts (Typical)	
Magnesium (Commercially Pure)	-1.75	More Active
Zinc	-1.1	
Aluminium Alloy (5% Zinc)	-1.05	
Aluminium (Commercially Pure)	-0.8	
Mild Steel (Clean & Shiny)	-0.5 to -0.8	
Mild Steel (Rusted)	-0.2 to -0.5	
Cast Iron (Not Graphitized)	-0.5	
Lead	-0.5	
Mild Steel in Concrete	-0.2	
Copper, Brass, Bronze	-0.2	
High Silicon Cast Iron	-0.2	
Mill Scale on Steel	-0.2	
Carbon, Graphite, Coke	+0.4	More Noble

TABLE 3 • Galvanic Series w.r.t. Cu:CuS0$_4$ Electrode

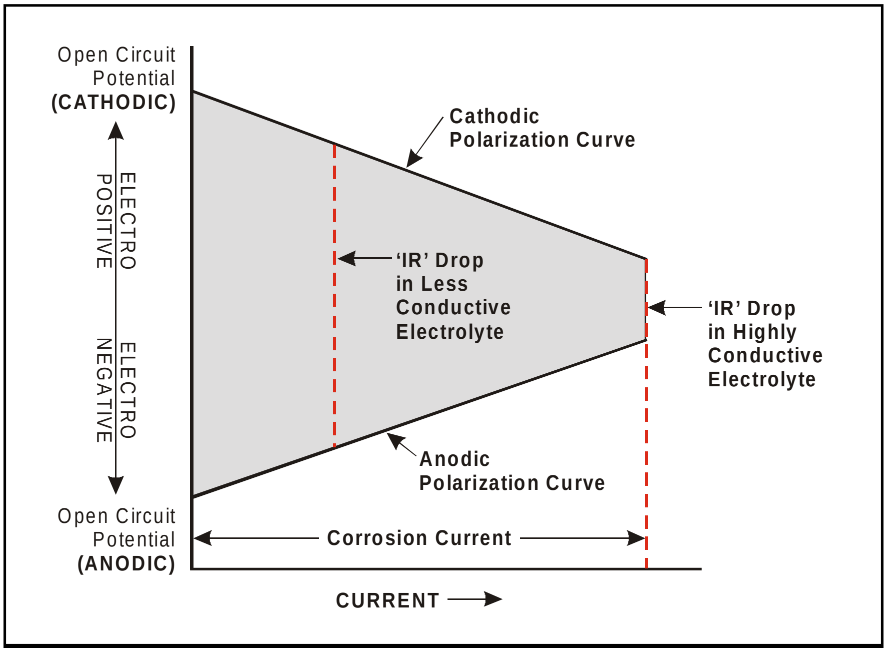


FIGURE 3 • Evan's Diagram

One other important phenomenon in the corrosion mechanism is polarization of the electrodes. Without polarization the majority of metals immersed in an electrolyte would corrode very rapidly. Polarization must be examined more carefully if a clear understanding of the control of corrosion processes is desired.

In a galvanic cell using zinc and copper in sea water, zinc is the anode and copper is the cathode. If these two metals are not in metallic contact with one another, no current flows in the cell and the metals are open circuited. Using suitable measuring probes, the open circuit potential of the anode and cathode can be determined. When the metallic circuit is closed, a corrosion process commences and a corrosion current flows from the anode through the electrolyte to the cathode. This current flow causes polarization of these two surfaces which results in a reduced potential difference between them. This process can be shown in an idealized fashion in what is called an Evan's Diagram (Figure 3).

Figure 3 indicates the open circuit potentials of the cathode and anode and shows how polarization tends to bring these two potentials closer together as the current flow increases. If a galvanic cell is short circuited, as is usually the case in naturally occurring corrosion situations, the anode and cathode potentials come very close together and are separated by the potential drop through the electrolyte caused by the passage of current (IR drop).

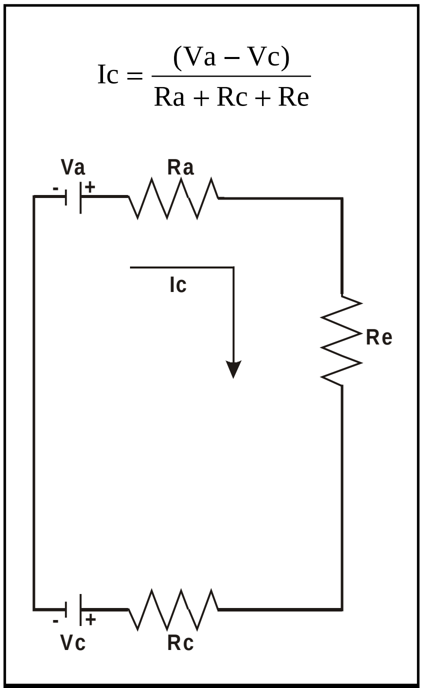
In highly conductive electrolytes, the IR drop is small and the corrosion current is large. In poorly conducting solutions, the equilibrium condition would occur at smaller current flows with less polarization on the anodes and cathodes. Such a situation is described by the dotted line drawn between the polarization curves. In the diagram shown, the flow of corrosion currents affects the potential of both the anode and cathode.

The equivalent electrical circuit of any corrosion cell is depicted in Figure 4. The anode and cathode solution potentials are modelled by the voltage sources Va and Vc respectively. The anode to cathode electrical resistance through the electrolyte is depicted as Re and polarization effects are accounted for by Ra and Rc. A corrosion current Ic is determined by:

$$\frac{(Va - Vc)}{Ra + Rc + Re} \tag{3}$$

Actual metal loss at the anode can be determined by the corrosion current (Ic), Faraday's equivalent for the particular metal of interest and the time the current is allowed to continue. For example, 1A of current discharging for one year from a piece of steel will dissolve (corrode) 20-22 lb. of metal. Conventional corrosion mitigation techniques attempt to minimize or halt this corrosion current.

To this point, only dissimilar metal corrosion has been considered. However, similar processes occur on a single sample of metal. A metal surface



$$Ic = \frac{(Va - Vc)}{Ra + Rc + Re}$$

FIGURE 4 • Simple Electrical Model of a Corrosion Cell in contact with an aqueous solution has areas on its surface that differ from one another in solution potential and are thus tiny anodes and cathodes. These differences are due to many causes, such as residual stresses, impurities in the metal, grain orientation, differences in metal ion concentration, thermal effects, and so on. The anodes corrode and the cathodes do not. A corrosion cell can only exist if there is a cathode and anode connected by a metallic path, with the cathode and anode, in a common electrolyte.

FORMS OF CORROSION

As previously mentioned, all forms of corrosion require the following minimum conditions: an anode, a cathode, a conductive electrolyte, and a metallic connection between the anode and cathode.

Although the basic mechanism is similar for all corrosion attack, variations of the corrosion cell parameters results in many different forms. The following is a list of the eleven most common types:

- dissimilar metal
- pitting corrosion
- de-alloying corrosion (corrosion attack to one constituent of the alloy)
- intergranular corrosion (attack at the grain boundaries of metals)
- stress corrosion cracking
- corrosion fatigue
- caustic embrittlement
- fretting corrosion
- crevice corrosion
- cavitation & impingement corrosion
- general attack

Information on these types of corrosion can be obtained from a number of corrosion textbooks.

CORROSION MITIGATION TECHNIQUES

Corrosion prevention systems minimize or stop the corrosion current or Ic (determined by Equation 3). Each type of protection changes or eliminates some component of the corrosion cell. Often two or more techniques are utilized simultaneously to mitigate a corrosion problem.

Protective Coatings

Protective coatings attempt to isolate the structure from the surrounding environment (electrolyte). The corrosion current Ic can now be defined as:

$$\frac{Va - Vc}{Ra + Rc + Re + Rp} \qquad (4)$$

where: Rp = the effective coating resistance

If the value of Rp is very large, as in the case of good quality coatings, the corrosion current decreases to a small value. In general, coating a structure is the only economical method of preventing atmospheric (non-immersed) corrosion.

Any small void in the coating is generally anodic to the remainder of the surface and can cause rapid corrosion perforation of the structure in immersed service. Frequently, coating protection schemes are supplemented by cathodic protection. Zinc rich paints and galvanizing provide a degree of cathodic protection.

Cathodic Protection

Cathodic protection combats corrosion by impressing an electrical current to the structure, ensuring the entire metal becomes a cathode. The electrical current changes the solution potential of the cathodes to a value at least as negative as the anodes. As can be seen from the equation:

$$Ic = \frac{(Va - Vc)}{Ra + Rc + Re} \qquad (5)$$

if Va = Vc the corrosion current becomes zero. In addition to minimizing the potential difference of the anodes and cathodes, the protective current also increases the value of Rc, the effective polarization resistance.

Cathodic protection can be implemented by either a sacrificial or impressed current system. A sacrificial scheme utilizes a more electronegative metal than the structure while the impressed current system requires a rectifier and semi-inert electrode.

Inhibitors

Chemical inhibitors attempt to polarize the anode and/or cathode of the corrosion cell. Again, this increase in the effective resistance of Ra and/or Rc results in a lower corrosion current. The use of inhibitors is generally restricted to “closed” systems.

Metallurgical Alloying

Additions of certain elements to metals can increase their corrosion resistance dramatically. Additions of chromium to steel produce the stainless steel alloys. The chromium additions produce corrosion products on the surface of the metal, which effectively isolates the structure from the environment. When stainless steel alloys do corrode, the usual mechanism of destruction is pitting due to local protective film breakdown. They are particularly vulnerable to pitting attack in solutions containing chlorides.