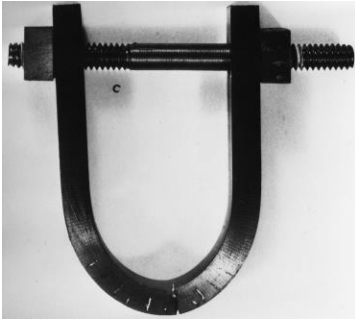


## Corrosion

- \*Why does corrosion occur?
- \*What metals are most likely to corrode?
- \*How do temperature and environment affect corrosion rate?
- \*How do we suppress corrosion?



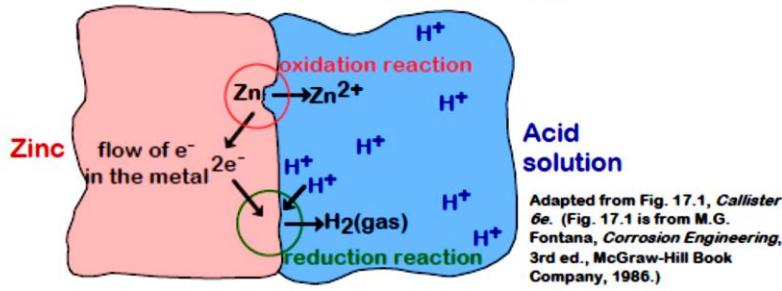
*Photograph showing a bar of steel that has been bent into a ‘horseshoe’ shape using a nut-and-bolt assembly. While immersed in seawater, stress corrosion cracks formed along the bend at those regions where the tensile stresses are the greatest.*

To one degree or another, most materials experience some type of interaction with a large number of diverse environments. Often, such interactions impair a material’s usefulness as a result of the deterioration of its mechanical properties (e.g., ductility and strength), other physical properties, or appearance. Occasionally, to the chagrin of a design engineer, the degradation behavior of a material for some application is ignored, with adverse consequences. Deteriorative mechanisms are different for the three material types. In metals, there is actual material loss either by dissolution (**corrosion**) or by the formation of nonmetallic scale or film (*oxidation*). Ceramic materials are relatively resistant to deterioration, which usually occurs at elevated temperatures or in rather extreme environments; the process is frequently also called corrosion. For polymers, mechanisms and consequences differ from those for metals and ceramics, and the term **degradation** is most frequently used. Polymers may dissolve when exposed to a liquid solvent, or they may absorb the solvent and swell; also, electromagnetic radiation (primarily ultraviolet) and heat may cause alterations in their molecular structure. Corrosion is defined as the destructive and unintentional attack of a metal; it is electrochemical and ordinarily begins at the surface. The problem of metallic corrosion is one of significant proportions; in economic terms, it has been estimated that approximately 5% of an industrialized nation’s income is spent on corrosion prevention and the maintenance or replacement of products lost or contaminated as a result of corrosion reactions. The consequences of corrosion are all too common. Familiar examples include the rusting of automotive body panels and radiator and exhaust components.

Corrosion processes are occasionally used to advantage. For example, etching procedures, make use of the selective chemical reactivity of grain boundaries or various microstructural constituents. Also, the current developed in dry-cell batteries is a result of corrosion processes.

# CORROSION OF ZINC IN ACID

- Two reactions are necessary:
  - oxidation reaction:  $Zn \rightarrow Zn^{2+} + 2e^{-}$
  - reduction reaction:  $2H^{+} + 2e^{-} \rightarrow H_2(\text{gas})$

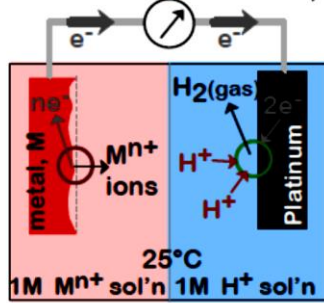


- Other reduction reactions:
  - in an acid solution:  $O_2 + 4H^{+} + 4e^{-} \rightarrow 2H_2O$
  - in a neutral or base solution:  $O_2 + 2H_2O + 4e^{-} \rightarrow 4(OH)^{-}$

# STANDARD HYDROGEN (EMF) TEST

- Two outcomes:

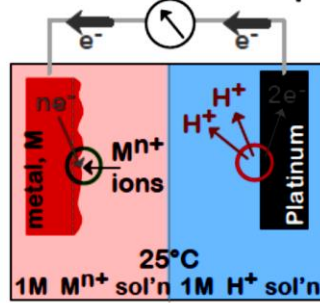
--Metal sample mass ↓



--Metal is the anode (-)

$$V_{\text{metal}}^0 < 0 \text{ (relative to Pt)}$$

--Metal sample mass ↑



--Metal is the cathode (+)

$$V_{\text{metal}}^0 > 0 \text{ (relative to Pt)}$$

Standard Electrode Potential



# STANDARD EMF SERIES

• EMF series

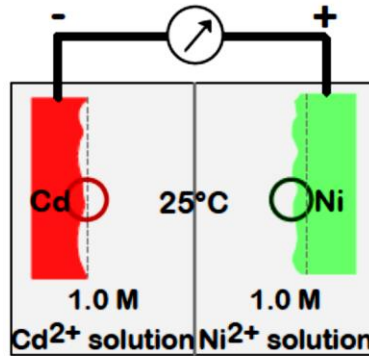
metal	$V_{\text{metal}}^{\circ}$
Au	+1.420 V
Cu	+0.340
Pb	-0.126
Sn	-0.136
Ni	-0.250
Co	-0.277
Cd	-0.403
Fe	-0.440
Cr	-0.744
Zn	-0.763
Al	-1.662
Mg	-2.262
Na	-2.714
K	-2.924

more cathodic ↑  
more anodic ↓

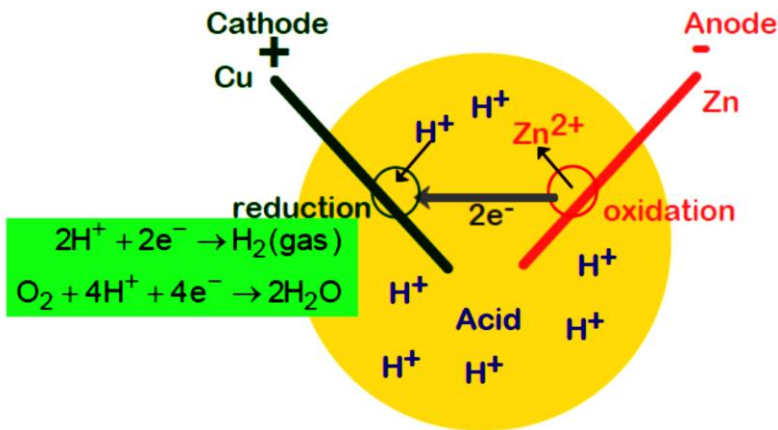
$\Delta V^{\circ} = 0.153V$

Data based on Table 17.1, Callister 6e.

- Metal with smaller  $V_{\text{metal}}^{\circ}$  corrodes.
- Ex: Cd-Ni cell

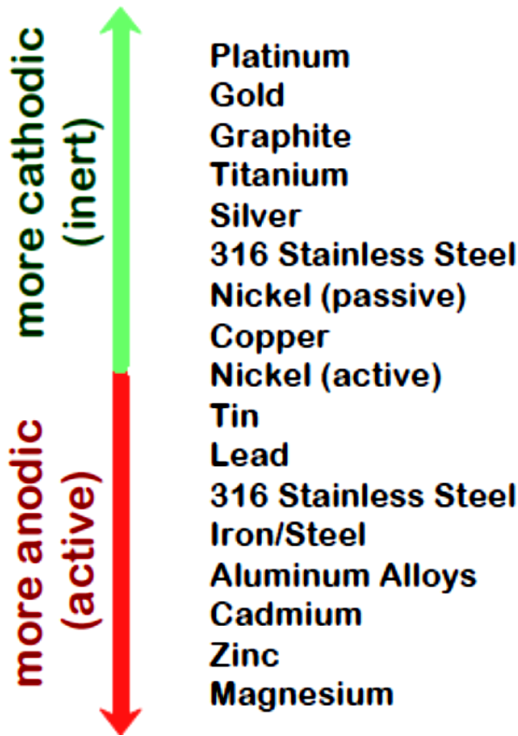


# CORROSION IN A GRAPEFRUIT



# GALVANIC SERIES

- Ranks the reactivity of metals/alloys in seawater



Based on Table 17.2, *Callister 6e*. (Source of Table 17.2 is M.G. Fontana, *Corrosion Engineering*, 3rd ed., McGraw-Hill Book Company, 1986.)



# FORMS OF CORROSION

- **Uniform Attack**  
Oxidation & reduction occur uniformly over surface.
- **Selective Leaching**  
Preferred corrosion of one element/constituent (e.g., Zn from brass (Cu-Zn)).
- **Intergranular**  
Corrosion along grain boundaries, often where special phases exist.
- **Stress corrosion**  
Stress & corrosion work together at crack tips.
- **Erosion-corrosion**  
Break down of passivating layer by erosion (pipe elbows).
- **Pitting**  
Downward propagation of small pits & holes.
- **Galvanic**  
Dissimilar metals are physically joined. The more anodic one corrodes. (see Table 17.2) Zn & Mg very anodic.
- **Crevice**  
Between two pieces of the same metal.

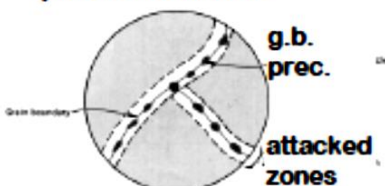
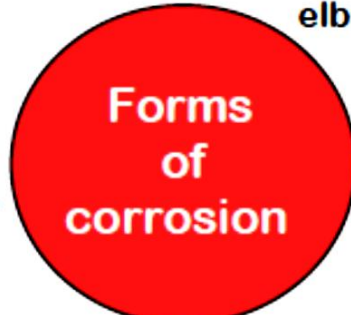


Fig. 17.9, *Callister 6e*.

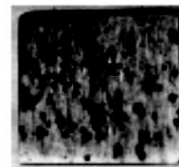


Fig. 17.8, *Callister 6e*. (Fig. 17.8 from M.G. Fontana, *Corrosion Engineering*, 3rd ed., McGraw-Hill Book Company, 1986.)



Fig. 17.6, *Callister 6e*. (Fig. 17.6 is courtesy LaQue Center for Corrosion Technology, Inc.)

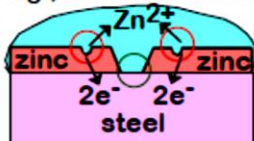


# CONTROLLING CORROSION

- **Self-protecting metals!**
  - Metal ions combine with O to form a thin, adhering oxide layer that slows corrosion.
- **Reduce T (slows kinetics of oxidation and reduction)**
- **Add inhibitors**
  - Slow oxidation/reduction reactions by removing reactants (e.g., remove O<sub>2</sub> gas by reacting it w/an inhibitor).
  - Slow oxidation reaction by attaching species to the surface (e.g., paint it!).
- **Cathodic (or sacrificial) protection**
  - Attach a more anodic material to the one to be protected.

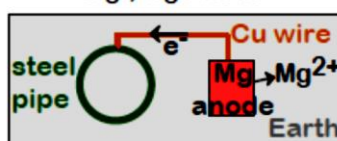


e.g., zinc-coated nail



Adapted from Fig. 17.14, Callister 6e.

e.g., Mg Anode



Adapted from Fig. 17.13(a), Callister 6e. (Fig. 17.13(a) is from M.G. Fontana, *Corrosion Engineering*, 3rd ed., McGraw-Hill Book Co., 1986.)

- Corrosion occurs due to:
  - the natural tendency of metals to give up electrons.
  - electrons are given up by an **oxidation** reaction.
  - these electrons then are part of a **reduction** reaction.
- Metals with a more negative **Standard Electrode Potential** are more likely to corrode relative to other metals.
- The **Galvanic Series** ranks the reactivity of metals in seawater.
- Increasing T speeds up oxidation/reduction reactions.
- Corrosion may be controlled by:
  - using metals which form a protective oxide layer
  - reducing T
  - adding inhibitors
  - painting
  - using cathodic protection.

# FORMS OF CORROSION

It is convenient to classify corrosion according to the manner in which it is manifest. Metallic corrosion is sometimes classified into eight forms: uniform, galvanic, crevice, pitting, intergranular, selective leaching, erosion–corrosion, and stress corrosion.

The causes and means of prevention of each of these forms are discussed briefly. In addition, we have elected to discuss the topic of hydrogen embrittlement in this section. Hydrogen embrittlement is, in a strict sense, a type of failure rather than a form of corrosion; however, it is often produced by hydrogen that is generated

from corrosion reactions:

## UNIFORM ATTACK

Uniform attack is a form of electrochemical corrosion that occurs with equivalent intensity over the entire exposed surface and often leaves behind a scale or deposit. In a microscopic sense, the oxidation and reduction reactions occur randomly over the surface. Some familiar examples include general rusting of steel and iron and the tarnishing of silverware. This is probably the most common form of corrosion. It is also the least objectionable because it can be predicted and designed for with relative ease.

## GALVANIC CORROSION

**Galvanic corrosion** occurs when two metals or alloys having different compositions are electrically coupled while exposed to an electrolyte. The rate of galvanic attack depends on the relative anode-to-cathode surface areas that are exposed to the electrolyte, and the rate is related directly to the cathode–anode area ratio; that is, for a given cathode area, a smaller anode will corrode more rapidly than a larger one. A number of measures may be taken to significantly reduce the effects of galvanic corrosion. These include the following:

1. If coupling of dissimilar metals is necessary, choose two that are close together in the galvanic series.
2. Avoid an unfavorable anode-to-cathode surface area ratio; use an anode area as large as possible.
3. Electrically insulate dissimilar metals from each other.
4. Electrically connect a third, anodic metal to the other two; this is a form of **cathodic protection**, discussed presently.

## CREVICE CORROSION

Electrochemical corrosion may also occur as a consequence of concentration differences of ions or dissolved gases in the electrolyte solution, and between two regions of the same metal piece. For such a *concentration cell*, corrosion occurs in the locale that has the lower concentration. A good example of this type of corrosion occurs in crevices and recesses or under deposits of dirt or corrosion products where the solution becomes stagnant and there is localized depletion of dissolved oxygen.

Corrosion preferentially occurring at these positions is called **crevice corrosion**.

## PITTING

**Pitting** is another form of very localized corrosion attack in which small pits or holes form. They ordinarily penetrate from the top of a horizontal surface downward in a nearly vertical direction. It is an extremely insidious type of corrosion, often going undetected and with very little material loss until failure occurs.

## INTERGRANULAR CORROSION

As the name suggests, **intergranular corrosion** occurs preferentially along grain boundaries for some alloys and in specific environments. The net result is that a macroscopic specimen disintegrates along its grain boundaries.

## SELECTIVE LEACHING

**Selective leaching** is found in solid solution alloys and occurs when one element or constituent is preferentially removed as a consequence of corrosion processes. The most common example is the dezincification of brass, in which zinc is selectively leached from a copper–zinc brass alloy. The mechanical properties of the alloy are significantly impaired, since only a porous mass of copper remains in the region that has been dezincified. In addition, the material changes from yellow to a red or copper color. Selective leaching may also occur with other alloy systems in which aluminum, iron, cobalt, chromium, and other elements are vulnerable to preferential removal.

## EROSION–CORROSION

**Erosion–corrosion** arises from the combined action of chemical attack and mechanical abrasion or wear as a consequence of fluid motion. Virtually all metal alloys, to one degree or another, are susceptible to erosion–corrosion. It is especially harmful to alloys that passivate by forming a protective surface film; the abrasive action may erode away the film, leaving exposed a bare metal surface. If the coating is not capable of continuously and rapidly reforming as a protective barrier, corrosion may be severe.

Relatively soft metals such as copper and lead are also sensitive to this form of attack. Usually it can be identified by surface grooves and waves having contours that are characteristic of the flow of the fluid. The nature of the fluid can have a dramatic influence on the corrosion behavior. Increasing fluid velocity normally enhances the rate of corrosion. Also, a solution is more erosive when bubbles and suspended particulate solids are present. Erosion–corrosion is commonly found in piping, especially at bends, elbows, and abrupt changes in pipe diameter—positions where the fluid changes direction or flow suddenly becomes turbulent. Propellers, turbine blades, valves, and pumps are also susceptible to this form of corrosion. Figure 16.20 illustrates the impingement failure of an elbow fitting. One of the best ways to reduce erosion–corrosion is to change the design to eliminate fluid turbulence and impingement effects. Other materials may also be utilized that inherently resist erosion. Furthermore, removal of particulates and bubbles from the solution will lessen its ability to erode.

### **STRESS CORROSION**

**Stress corrosion**, sometimes termed stress corrosion cracking, results from the combined action of an applied tensile stress and a corrosive environment; both influences are necessary. In fact, some materials that are virtually inert in a particular corrosive medium become susceptible to this form of corrosion when a stress is applied. Small cracks form and then propagate in a direction perpendicular to the stress (see the chapter-opening photograph for this chapter), with the result that failure may eventually occur. Failure behavior is characteristic of that for a brittle material, even though the metal alloy is intrinsically ductile. Furthermore, cracks may form at relatively low stress levels, significantly below the tensile strength. Most alloys are susceptible to stress corrosion in specific environments, especially at moderate stress levels. For example, most stainless steels stress corrode in solutions containing chloride ions, whereas brasses are especially vulnerable when exposed to ammonia.

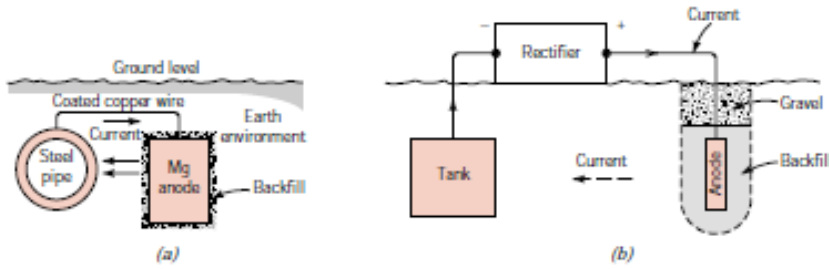
## **CORROSION PREVENTION**

Some corrosion prevention methods were treated relative to the eight forms of corrosion; however, only the measures specific to each of the various corrosion types were discussed. Now, some more general techniques are presented; these include material selection, environmental alteration, design, coatings, and cathodic protection. Perhaps the most common and easiest way of preventing corrosion is through the judicious selection of materials once the corrosion environment has been characterized. Standard corrosion references are helpful in this respect. Here, cost may be a significant factor. It is not always economically feasible to employ the material that provides the optimum corrosion resistance; sometimes, either another alloy and /or some other measure must be used. Changing the character of the environment, if possible, may also significantly influence corrosion. Lowering the fluid temperature and/or velocity usually produces a reduction in the rate at which corrosion occurs. Many times increasing or decreasing the concentration of some species in the solution will have a positive effect; for example, the metal may experience passivation. **Inhibitors** are substances that, when added in relatively low concentrations to the environment, decrease its corrosiveness. Of course, the specific inhibitor depends both on the alloy and on the corrosive environment. There are several mechanisms that may account for the effectiveness of inhibitors. Some react with and virtually eliminate a chemically active species in the solution (such as dissolved oxygen). Other inhibitor molecules attach themselves to the corroding surface and interfere with either the oxidation or the reduction reaction, or form a very thin protective coating. Inhibitors are normally used in closed systems such as automobile radiators and steam boilers. Several aspects of design consideration have already been discussed, especially with regard to galvanic and crevice corrosion, and erosion–corrosion. In addition, the design should allow for complete drainage in the case of a shutdown, and easy washing. Since dissolved oxygen may enhance the corrosivity of many solutions, the design should, if possible, include provision for the exclusion of air.

Physical barriers to corrosion are applied on surfaces in the form of films and coatings. A large diversity of metallic and nonmetallic coating materials are available. It is essential that the coating maintain a high degree of surface adhesion, which undoubtedly requires some preapplication surface treatment. In most cases, the coating must be virtually nonreactive in the corrosive environment and resistant to mechanical damage that exposes the bare metal to the corrosive environment. All three material types—metals, ceramics, and polymers—are used as coatings for metals.

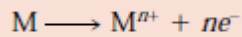
### **CATHODIC PROTECTION**

One of the most effective means of corrosion prevention is **cathodic protection**; it can be used for all eight different forms of corrosion as discussed above, and may,

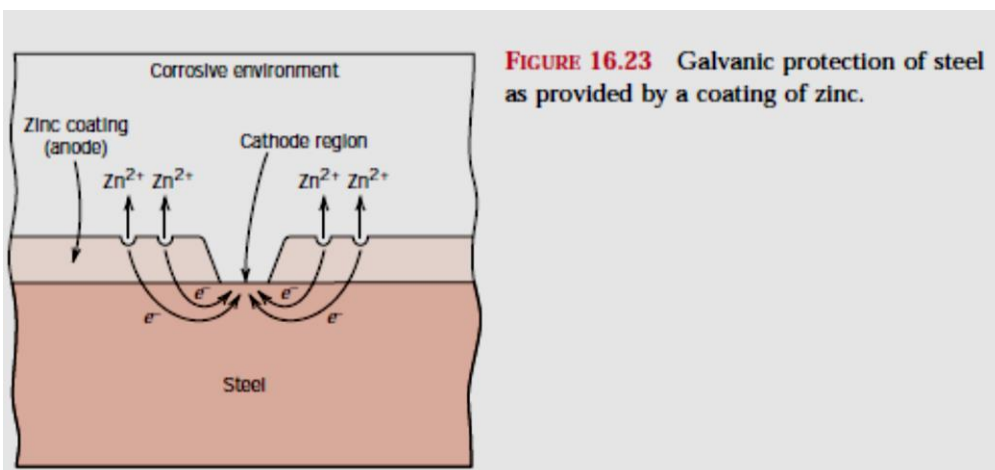


**FIGURE 16.22** Cathodic protection of (a) an underground pipeline using a magnesium sacrificial anode, and (b) an underground tank using an impressed current. (From M. G. Fontana, *Corrosion Engineering*, 3rd edition. Copyright © 1986 by McGraw-Hill Book Company. Reproduced with permission.)

in some situations, completely stop corrosion. Again, oxidation or corrosion of a metal M occurs by the generalized reaction.



One cathodic protection technique employs a galvanic couple: the metal to be protected is electrically connected to another metal that is more reactive in the particular environment. The latter experiences oxidation, and, upon giving up electrons, protects the first metal from corrosion. The oxidized metal is often called a **sacrificial anode**, and magnesium and zinc are commonly used as such because they lie at the anodic end of the galvanic series. The process of *galvanizing* is simply one in which a layer of zinc is applied to the surface of steel by hot dipping. In the atmosphere and most aqueous environments, zinc is anodic to and will thus cathodically protect the steel if there is any surface damage (Figure 16.23). Any corrosion of the zinc coating will proceed at an extremely slow rate because the ratio of the anode-to-cathode surface area is quite large.



For another method of cathodic protection, the source of electrons is an impressed current from an external dc power source, as represented in Figure 16.22b for an underground tank. The negative terminal of the power source is connected to the structure to be protected. The other terminal is joined to an inert anode (often graphite), which is, in this case, buried in the soil; high-conductivity backfill material provides good electrical contact between the anode and surrounding soil. A current path exists between the cathode and anode through the intervening soil, completing the electrical circuit. Cathodic protection is especially useful in preventing corrosion of water heaters, underground tanks and pipes, and marine equipment.